1975

Stereochemistry and Mechanisms of Reactions of Silacyclobutanes.

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STEREOCHEMISTRY AND MECHANISMS OF REACTIONS OF SILACYCLOBUTANES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by
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B.S., Northeast Louisiana State College, 1969
August, 1975

ACKNOWLEDGMENT

This work has been accomplished under the direction of Professor Frank K. Cartledge, to whom I am grateful for the knowledge and understanding of chemistry which he has imparted to me and for the patience he has shown.

I would like to express my appreciation to my wife, Faye, whose confidence in me has not waivered and whose patience is never-ending. Also to my parents, for the encouragement and financial support provided me, I am eternally grateful.

In addition, I would like to express my gratitude to Louisiana State University for financial support rendered to me as a research assistant and to the Cities Service Education Foundation for supporting me in basic research.

Finally, I would like to acknowledge the following contributions: Ms. Joanne Wolcott, Dr. Peter Chen, Dr. Benedict Ho, and Mr. Jack Fayssoux for their friendship, interesting discussions, and technical assistance; Dr. N. S. Bhacca for assistance in interpretation of NMR spectra; Ms. Paula Moses, Mr. Ralph Seab, Mr. David Latour, and Mr. John Martin, technical assistance; the Charles E. Coates Memorial Fund of the L. S. U. Foundation (donated by Dr. George H. Coates), financial provision in the production of this dissertation.

B. Gary McKinnie
June, 1975

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ABSTRACT

The stereochemistries of a number of nucleophilic displacement reaction of 1-substituted-1,2-dimethyl-1-silacyclobutanes have been investigated. Retention of configuration was observed upon reduction, with $LiAlH_4$ in ether, of the methoxide, fluoride, and chloride derivatives, and also upon displacement of chloride with Grignard reagents. Reaction of the p-anisyl derivative with bromine is more complicated, giving different isomeric product ratios at different temperatures. The stereochemical studies are interpretable either in terms of an increased barrier to inversion at silicon due to increased angle strain, or as formation of a pentacoordinate species that undergoes permutational isomerization.

The geometric isomers of 1,2-dimethyl-1-silacyclobutane have been subjected to solvolysis in alkaline aqueous methanol. Ring-opened products have been isolated, and evidence has been accumulated indicating that ring opening and hydride displacement occur at competitive rates. No cis or trans isomerization occurs during the course of the reaction. Kinetic and stereochemical results of hydride displacement are interpretable in terms of either a rate-determining formation of a pentacoordinate intermediate or direct displacement.

The kinetics of isomerization of cis-1-chloro-1,2-dimethyl-1-silacyclobutane with hexamethylphosphoric triamide (HMPT) has been investigated. The reaction is first-order in chlorosilane and second-order in HMPT at low HMPT concentrations but first-order at

high HMPT concentrations. Halide-halide exchange accompanies isomerization. The results indicate the mechanism of isomerization to be a two-step displacement of halide ion to give a pentacoordinate intermediate that is either symmetrical or able to undergo permutational isomerization.

CHAPTER I

INTRODUCTION

With the increased interest in recent years in reactions of organosilicon compounds, greater emphasis has been placed on determination of the mechanisms of these reactions. This field has experienced a tremendous growth, due primarily to the study of optically active triorganosilanes by Sommer and co-workers.[1] Yet the mechanisms of many reactions are not known with any certainty, and recently, the mechanisms of some reactions that were previously believed to be well established have been questioned.[2-4]

Although carbon and silicon are congeners, many differences are found in the mechanisms of similar reactions due to the reluctance of silicon to form π-bonded species[5] or three-coordinate species.[6] Further, silicon appears to follow some mechanistic pathway that is not possible for carbon, as is evident by the much greater reactivity of bridgehead chlorosilanes *vs.* analogous carbon systems.[7]

Nucleophilic substitution reactions of triorganosilanes have been extensively studied. Three basic mechanisms appear to operate: S_N2-Si, S_Ni-Si, and formation of extra-coordinate intermediates.[1]

The S_N2-Si mechanism is analogous to S_N2 reactions for carbon. Initial back-side attack leads to a transition state in which simultaneous bond-breaking and bond-making occur. Inversion of configuration results. S_N2-Si reactions occur usually when the conjugate acid of the leaving group has a pKa less than about 6, providing the

entering group is more basic than the leaving group.[8] The nature of the solvent appears to have little effect on the mechanism.

If the pKa of the conjugate acid of the leaving group is greater than 10 then the usual stereochemistry is retention of configuration.[1,9] These reactions proceed through the S_Ni-Si mechanism which involves quasi-cyclic rate-controlling transition states which are generally four-centered but also may be three-, five-, or six-centered.[10] The electrophilic part, E, of the attacking nucleophile, Y, assists in pulling off the leaving group X (Figure 1-1). Participation of silicon's 3d orbitals may occur to lower the

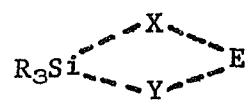
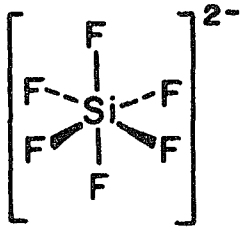


Figure 1-1. Transition state for S_Ni-Si mechanism.

free energy of the transition state and may even permit the S_Ni-Si mechanism to occur through an unstable pentacoordinate intermediate.[1]

The presence of extra-coordinate intermediates in reactions of silicon compounds has been proposed innumerable times. Participation of silicon's 3d orbitals is usually invoked to explain such a mechanism, while the lack of participation of the carbon d-orbitals is invoked to point out the inability of carbon to form such intermediates. However, recently a reaction at carbon that occurred with retention of configuration was suggested to proceed through a pentacoordinate intermediate.[11] Indeed there is a number of stable five- and six-coordinate silicon compounds. The hexafluorosilicate

anion[12] (1), triptych-siloxazolidines[13,14] (2), and alkylammonium siliconate salts derived from 1,2-diols[15,16] (3) are typical. Yet



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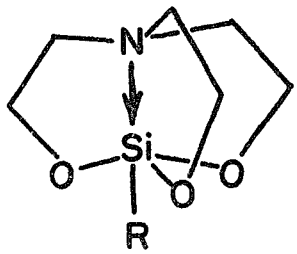

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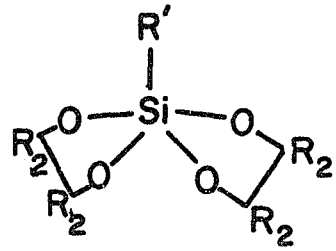

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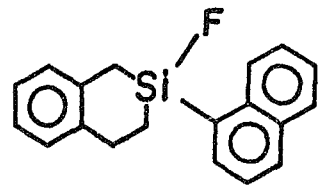
their existence by no means proves the presence of such intermediates in reactions of triorganosilanes. The majority of the evidence that implies the presence of extra-coordinate intermediates is from kinetic data. For example, the small differences in rates of reactions with different leaving groups have been suggested as evidence for slow rate-determining formation of pentacoordinate intermediates.[3,4] Definite proof of the presence of such intermediates, however, has not been presented.

The above discussion, at least with respect to S_N2-Si and S_Ni-Si reactions, is somewhat oversimplified. Stereochemical crossover from inversion to retention or retention to inversion has been observed in a number of reactions and has been shown to be a function of the nucleophile, the leaving group, and the solvent.[9,10,17] Even subtle changes in the system can apparently change the mechanism. Consider, for example, the reduction of α-napthylphenylmethylfluorosilane

which occurs with inversion of configuration,[1] while the reduction of 4 occurs with racemization.[18]



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Systems investigated until recently are basically very similar with respect to silane structure and thus probably have not revealed some perhaps common stereochemical possibilities. Recent investigations by Sommer with the 1-silaacenaphthene system, in which the silicon atom is incorporated into a strained ring, have already shown one such new possibility.[19]

A promising system in which to gain new information is silacyclobutanes. The chemistry of this ring system has been studied extensively and has recently been reviewed.[20] Due mainly to the work of Damrauer, silacyclobutanes may now be prepared in high yields.[21] Silacyclobutanes are more reactive than acyclic silanes and cyclobutanes. They often undergo ring opening and are thermally unstable, polymerizing slowly even at room temperature to polymers that contain silicon in the main chain.[22] Undoubtedly the relief of ring strain is the driving force for their increased reactivity. The C-Si-C angle has been determined to be 80° in both 1,1-dimethyl- and 1,1-dichlorosilacyclobutane.[23]

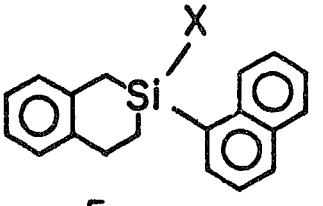
Only recently have studies been undertaken with substituted silacyclobutanes in which geometric isomerism is possible. Dubac and co-workers prepared a number of derivatives of 1,2- and 1,3-dimethyl-1-silacyclobutane and studied the stereochemistry of some reactions.[24-27] All reactions that were stereospecific proceeded with retention. Reactions of the 1-chlorosilacyclobutanes with alcohols and amines were not stereospecific but rather stereoselective, and the results were interpreted in terms of an extra-coordinate intermediate that underwent "stereomutation".[26]

The results of further investigations of reactions of 1,2-dimethylsilacyclobutanes will be presented herein. Significant conclusions concerning the mechanisms of nucleophilic substitution at silicon will be made.

CHAPTER II

STEREOCHEMISTRY OF REACTIONS OF SILACYCLOBUTANES

The stereochemistry of reactions at asymmetric silicon atoms has been studied in a number of different chiral organosilane systems. Aside from acyclic systems, such as the α-naphthylphenylmethylsilane system,[1,28] stereochemical studies have been made with the trihydro-2-silanaphthalene system[18,29,30] (5), and, to a much less extent, with



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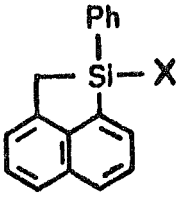
the 4-tert-butyl-1-silacyclohexane, and 1,2-disilacyclohexane systems.[31,32] The results, as previously discussed, have indicated that the stereochemical outcome depends on the nature of the entering and leaving groups and sometimes the solvent, but not normally on organosilane structure. The first significant deviation from this type of behavior was recently reported by Sommer.[19] In the 1-phenyl-1-silaacenaphthene ring system (6) both inversion and



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retention are reasonable stereochemical possibilities, but only retention was observed, even in the reduction of the chloro derivative with $LiAlH_4$ in ether, which proceeds with predominant or complete inversion of configuration at Si in other chiral organosilanes. Sommer postulated that the stereochemical crossover from inversion to retention is associated with angle strain at Si, the 1-Np-Si-CH_2 angle in 6 being 93.4°.[19] This observation demanded confirmation in other angle strained systems that incorporate substituents with less electronic and steric influences. A system that met the requirements was the 1,2-dimethyl-1-silacyclobutane ring system.

Dubac and co-workers have reported the displacement of tert-butoxide from 2-methyl- and 3-methyl-1-silacyclobutanes by methylmagnesium iodide or n-butyllithium or $LiAlH_4$, all of these reactions being stereospecific with retention.[25,27] However, similar reactions involving displacement of alkoxide in nonstrained systems also proceed with retention.[1] The same authors reported the reduction of 1,2-dimethyl-1-chloro-1-silacyclobutane (7) by $LiAlH_4$ to be nonstereoselective.[25] Slow inversion of silicon hydrides induced by $LiAlH_4$ is known to occur and probably accounts for the reported nonstereoselective reduction.[33]

Of interest were the reactions of 1-chloro, 1-fluoro-, and 1-methoxy-1,2-dimethyl-1-silacyclobutane with $LiAlH_4$ in ethyl ether. The stereochemistry of these reactions has previously been thoroughly studied with other systems. The reduction of chlorosilanes normally proceeds with inversion of configuration regardless of the solvent or nature of the reducing reagents, the only exception being that

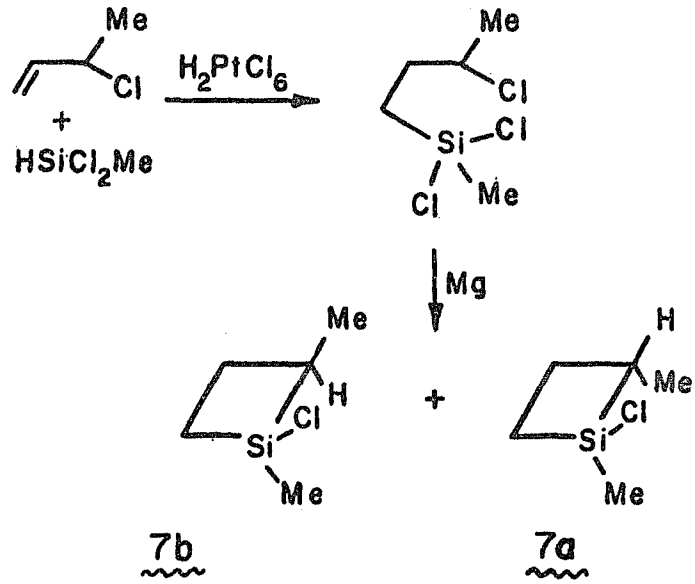
previously discussed and bridgehead chlorosilanes where inversion is not possible.[34]

The reduction of fluorosilanes is unusual in the respect that both inversion and retention of configuration have been observed even through the pKa of HF (3.2) is less than 6, and therefore inversion of configuration would be expected. Inversion occurred in the reduction of α-NpPhMeSiF with $LiAlH_4$ or i-Bu_2AlH in ethyl ether but retention was observed when the same compound was reduced in hexane with i-Bu_2AlH.[1,9] These facts, combined with the results obtained by Sommer with the silaacenaphthene system indicated that reduction of 1-fluoro-1,2-dimethyl-1-silacyclobutane (8) would probably proceed with retention of configuration. The observation by Corriu of racemization in the reduction by $LiAlH_4$ of 1-α-napthyl-2-fluoro-1,3,4-trihydro-2-silanaphthalene,[18] where Si is incorporated in a six-membered ring, necessitated the determination of the stereochemical outcome of the reduction of the fluoro derivative.

The reduction of 1-methoxy-1,2-dimethyl-1-silacyclobutane (9) would probably proceed with retention of configuration since acyclic alkoxysilanes give retention of configuration[1] and other displacement reactions of alkoxide from silacyclobutanes occur with retention.[25,27] Such a prediction requires confirmation however.

The preparation of 7 was carried out by the method previously reported[24] (Scheme 2-1). Ring closure by the method of Damrauer,[21]

SCHEME 2-1



using magnesium powder previously activated with ethylene bromide, afforded in 63% yield an 85:15 mixture, 7a and 7b, respectively, of cis- and trans-1-chloro-1,2-dimethyl-1-silacyclobutane.* Compound 7 gave slow isomerization on distillation at atmospheric pressure, but could be distilled at reduced pressure without a change in the isomeric ratio. This isomerization is probably due to a trace of ethyl ether, still present at high temperatures, which has previously been shown to give racemization of chlorosilanes.[35] The isomerization on distillation accounts for the various ratios of 7a and 7b used throughout this

*Throughout this work cis and trans are defined with respect to the methyl groups. Suffix a is added to the cis compounds and b to the trans. Isomeric ratios are always reported cis:trans.

work and for the apparent enrichment of a mixture in 7a by distillation previously reported by this group.[36]

Reduction of an 80:20 mixture of 7a and 7b with $LiAlH_4$ in diethyl ether (Reaction 2-1) gave an 80:20 mixture, 10a and 10b,

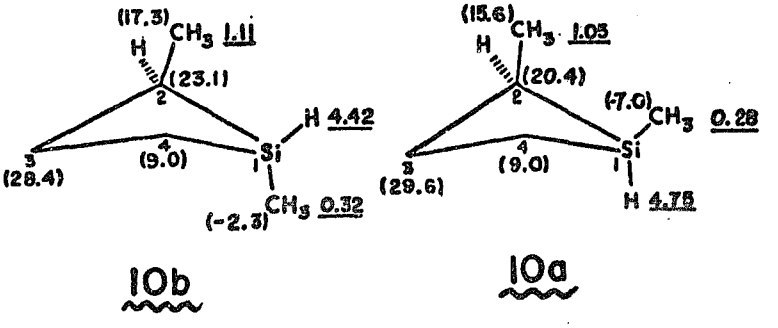
REACTION 2-1

7 10

respectively, the two isomers of 1,2-dimethyl-1-silacyclobutane, as determined by glpc. Similarly, reduction of a 60:40 mixture of 7 gave a 60:40 mixture of 10 indicating the reaction is stereospecific.

In order to determine the stereochemistry of the reaction, 10a and 10b were separated by preparative glpc. The structures of the two isomers were assigned from ^{1}H and ^{13}C NMR chemical shifts

(Figures 2-1 and 2-2). No attempt was made to judge the relative

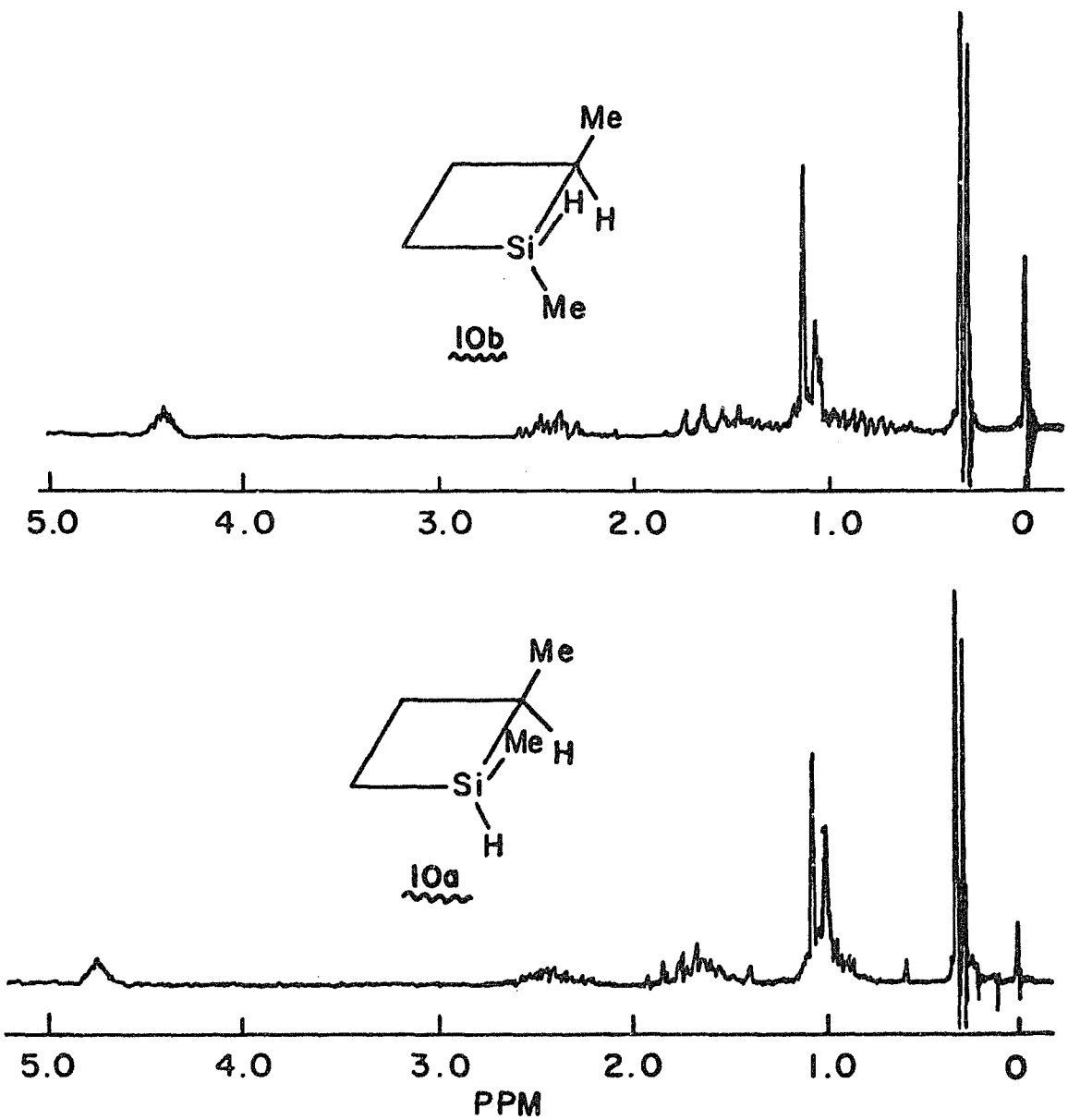


10b 10a

Figure 2-1. ^{1}H (underlined) and ^{13}C (in parentheses) chemical shifts for cis- and trans-1,2-dimethyl-1-silacyclobutane, in $CDCl_3$ relative to TMS.

stabilities of silacyclobutane conformers. The ring is known to be puckered but also to be flipping extremely rapidly on an NMR time scale.[23,37,38] In many substituted cycloalkanes substituents exert an influence on the chemical shifts of protons on an adjacent carbon that is stereospecific and greater when the substituent and proton are cis to one another than when they are trans.[39] Methyl groups generally show the effect of shielding cis protons on adjacent carbons,[40-43] and in the case of the trans isomer, 10b, shielding of the proton on Si by the cis C_2-Me gave rise to a resonance at substantially higher field (δ 4.42) than the Si-H of the cis isomer (δ 4.75). Also, the Si-Me and C_2-Me protons appeared at a higher field (slightly, but consistently) in the cis isomer. The proton

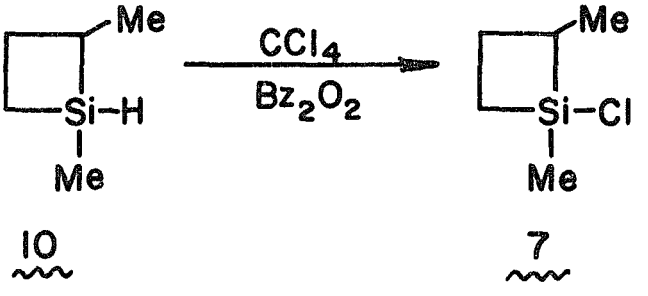
FIGURE 2-2. ^{1}H NMR spectra (100 MHz) of <u>trans</u>- and <u>cis</u>-1,2-dimethyl-1-silacyclobutane in $CDCl_3$.


Me
H
H
Si
Me
10b
5.0
4.0
3.0
2.0
1.0
0
Me
Me
H
Si
H
10a
5.0
4.0
3.0
2.0
1.0
0
PPM

on C_2 could not be resolved from the other ring protons so that no useful coupling constant data were available, nor could a nuclear Overhauser effect be determined. On these bases, 10a was assigned the cis structure and 10b the trans structure. The stereochemical assignments were confirmed by ^{13}C chemical shifts for which a reasonably close analogy to the present system exists in a study of methyl-substituted phosphetanes.[44] Steric interaction between the methyl groups of the cis isomer gave rise to resonances at higher field for both the Si-Me (δ -7.0) and the C_2-Me (δ 15.6) relative to the SiMe (δ -2.3) and C_2-Me (δ 17.3) of the trans isomer. This high field shift was also observed for the C_2 resonance of the cis isomer.

Free radical chlorination using CCl_4 and benzoyl peroxide was carried out on 10a to give 7a (Reaction 2-2). The reaction was

REACTION 2-2



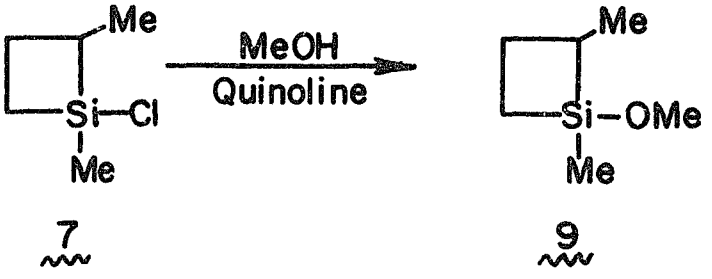
10 7

greater than 95% stereospecific as determined by NMR. Similarly, 10b gave 7b. Since this reaction goes through a silyl radical intermediate,[45,46] 10a was presumed to have arisen from 7a with

retention of configuration.[47-50] ^1H chemical shifts of the Si-Me groups in the chlorides offered additional evidence that 7a had the cis structure and 7b the trans structure. Due to shielding of the cis C_2-Me in 7a the Si-Me appeared at higher field (δ 0.55) than the Si-Me in 7b (δ 0.62). Perhaps surprisingly, the assignment meant that the original ring closure gave a substantially greater amount of the cis isomer than trans isomer, whereas conformational analysis indicates that methyl is appreciably larger than chlorine[51] and CNDO/2 calculations indicate the trans isomer is thermodynamically more stable [52] The stereochemical assignments were in accord with those made previously[24] and led to the firm conclusion that reduction of Si-Cl by $LiAlH_4$ in the silacyclobutane ring system proceeded with retention of configuration. The angle strain effect was thus confirmed.

Reaction of a 70:30 mixture of 7a and 7b respectively with methanol using quinoline as an acid acceptor (Reaction 2-3) gave a

REACTION 2-3



7 9

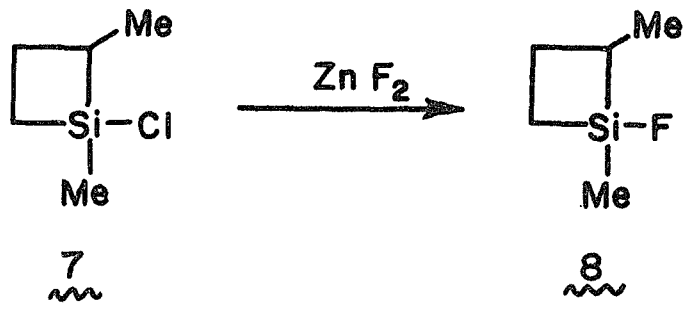
70:30 mixture, 9a and 9b respectively, of the two isomers of

1,2-dimethyl-1-methoxy-1-silacyclobutane. ^{1}H chemical shifts of the Si-Me groups indicated 9a had the cis structure, having a resonance at higher field than the trans isomer, 9b. The chemical shifts of the O-Me groups were not consistent with this assignment, the O-Me of 9a, where it is trans to the C_2-Me, appearing at higher field than the O-Me of 9b. The assignments of structures were the same as those proposed by Dubac and Mazerolles.[24,26]

Reduction of the 70:30 mixture of 9a and 9b with $LiAlH_4$ gave a 75:25 mixture of 10a and 10b. If the structural assignments of the isomers of 9 are correct then the reduction must have occurred with >90% retention of configuration, as anticipated.

In order to determine if the reduction of the fluoro derivative was stereospecific, 7 was reacted with zinc fluoride (Reaction 2-4) to give a 70:30 mixture, 8a and 8b respectively, of

REACTION 2-4



7 8

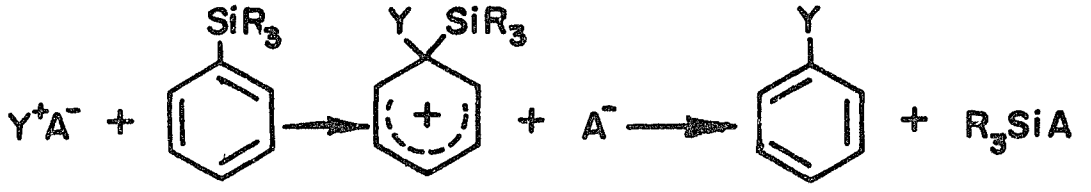
cis and trans-1-fluoro-1,2-dimethyl-1-silacyclobutane. The assignments of 8a as the cis isomer and 8b as the trans isomer were from the ^{1}H chemical shifts of the Si-Me groups and ^{19}F chemical

shifts, both being consistent and being based on reasoning similar to that applied to the hydrides. The reaction of the chloride with zinc fluoride was nonstereospecific since both a 70:30 and 50:50 mixture of 7a and 7b gave a 70:30 mixture of 8a and 8b.

Reduction of the 70:30 mixture of 8a and 8b with $LiAlH_4$ gave a 70:30 mixture of 10a and 10b respectively. Although no other ratio of 8a and 8b was available for reduction, it was evident that the reaction was stereospecific since the equilibrium ratio of 10a to 10b is known to be 46:54 respectively (see Chapter III). If the reaction were nonstereospecific the equilibrium ratio of 10 would probably have been formed. The results revealed that the racemization observed by Corriu in the reduction of the 6-membered cyclic fluorosilane is not characteristic of all cyclic silanes.

Since all reactions of strained cyclic silanes in which the stereochemistry was known occurred with predominant retention of configuration, the question remained as to whether any reactions of such systems would occur with inversion of configuration. If Sommer's postulate is correct, that the better the leaving group the greater the tendency for inversion of configuration,[18] then nucleophilic displacement of better leaving groups than chloride ion would possibly proceed with inversion. Such a leaving group was found in desilylation reactions which proceed through Wheland intermediates (Scheme 2-2).[53] Cleavage can be accomplished with

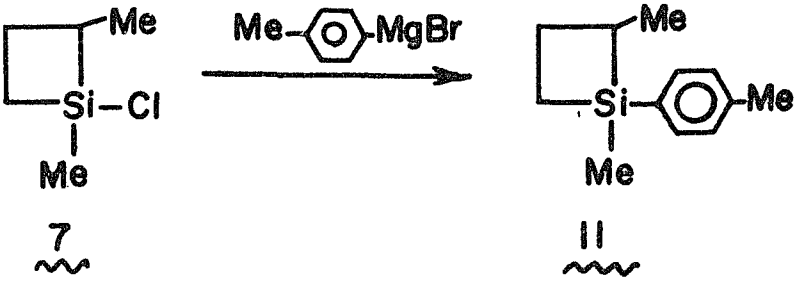
SCHEME 2-2



most of the reagents that give electrophilic aromatic substitution, and as expected, occur with inversion of configuration in the case of halogens.[54] The study of such reactions of silacyclobutanes is complicated, however, by ring opening.[20] Indeed, discoloration of bromine has been used as a test for silacyclobutanes although the products of the reaction have not been characterized.[55]

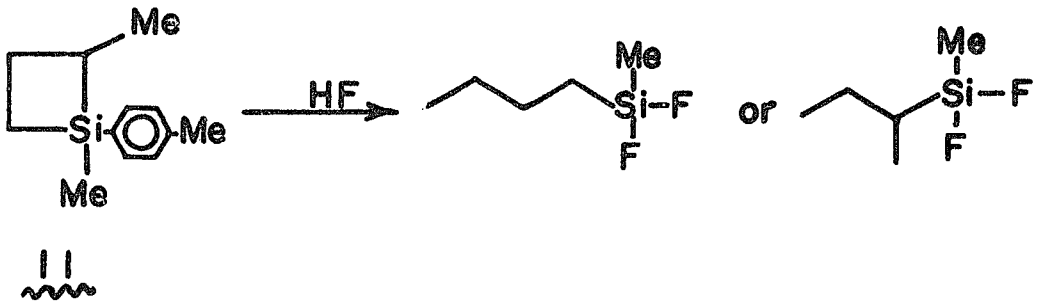
Reaction of a 50:50 mixture of 7a and 7b with p-tolylmagnesium bromide (Reaction 2-5) gave a 50:50 mixture, 11a and 11b, of the two

REACTION 2-5



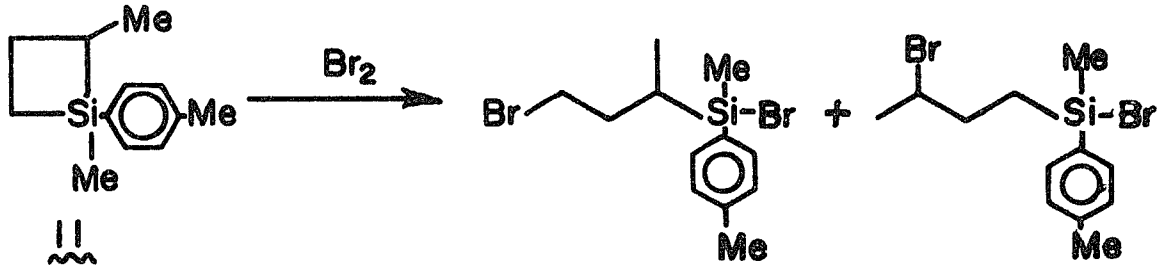
isomers of 1,2-dimethyl-1-p-tolyl-1-silacyclobutane. Reaction of 11 with hydrogen fluoride gave apparently either or both n-butyl and sec-butyldifluoromethylsilane (Reaction 2-6), and with

REACTION 2-6



bromine gave an apparent mixture of the ring opened products shown in Reaction 2-7. Although the products were not fully characterized,

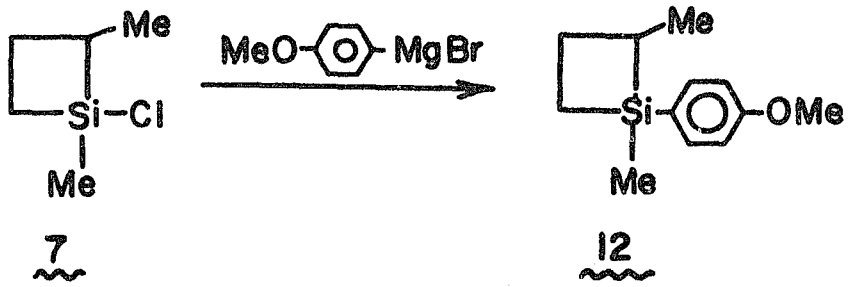
REACTION 2-7



the desired products with the ring intact definitely were not present in the products.

To facilitate electrophilic attack on the aromatic ring 1-p-anisyl-1,2-dimethyl-1-silacyclobutane, 12, was prepared. Reaction of a 50:50 mixture of 7a and 7b with p-anisylmagnesium bromide gave a 50:50 mixture of 12a and 12b (Reaction 2-8). Similarly, an 85:15

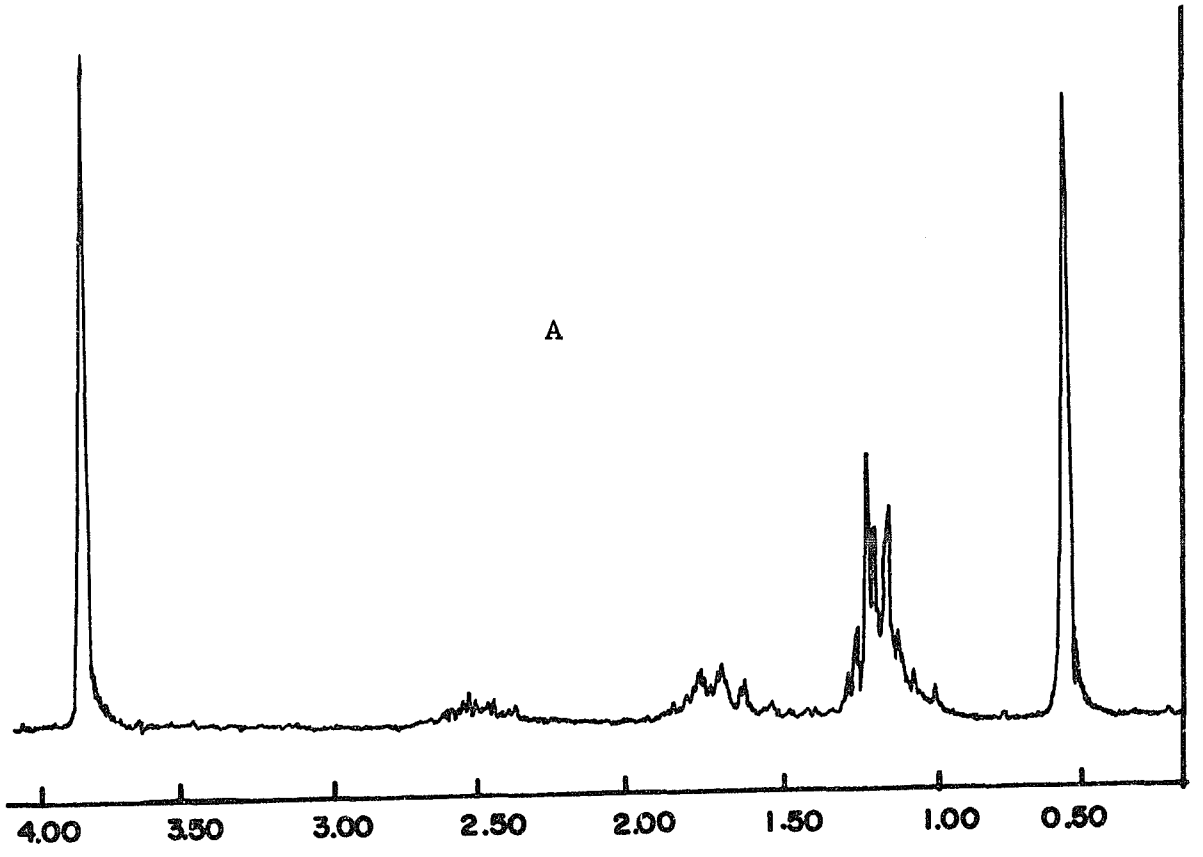
REACTION 2-8

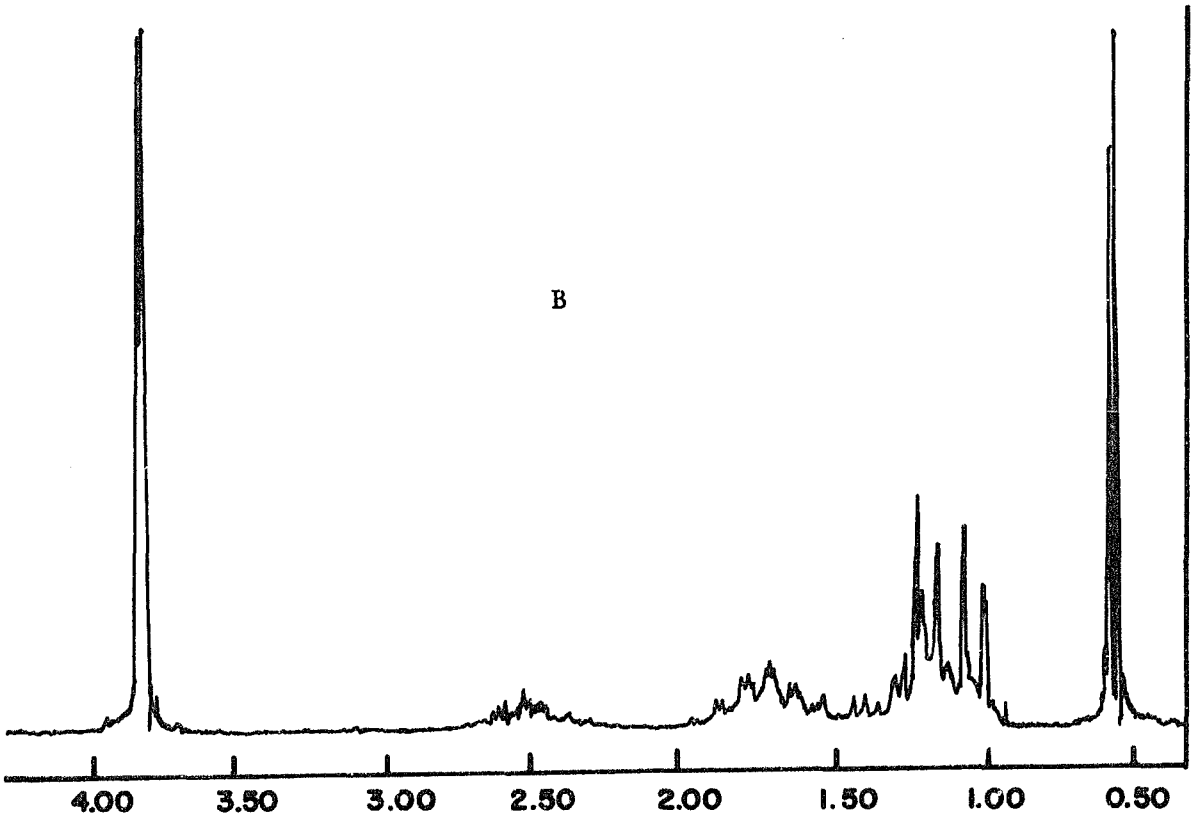


7 12

mixture of 7a and 7b respectively gave an approximate 85:15 mixture of 12a and 12b. The structures of the two isomers were assigned from their ^{1}H NMR spectra (Figure 2-3). The Si-Me of the cis isomer appears at a slightly higher field that the trans isomer. Also, the C_2-Me of the trans isomer, where it is cis to the aromatic ring, appears at substantially higher field than the C_2-Me of the cis isomer. Such diamagnetic anisotropic shifts are well known[39,56] and have previously been observed in phenyl substituted cyclic silanes.[32] A similar shift to higher field is observed for the C_2-Me of 11b. On these bases, 12a is assigned the cis structure and 12b the trans structure. The assignments mean that the displacement of chloride from 7 with the Grignard reagents proceeds with predominant retention of configuration. This is contrary to the stereochemistry normally observed in the reaction of Grignard reagents with chlorosilanes which usually occur with inversion.[29] However, aryl Grignards often fail to react with the sterically hindered chlorosilanes used in stereochemical studies[29] and thus little is known of the reactions. One chlorosilane has been shown to give predominant (56%) retention of configuration when reacted with phenylmagnesium bromide.[57]

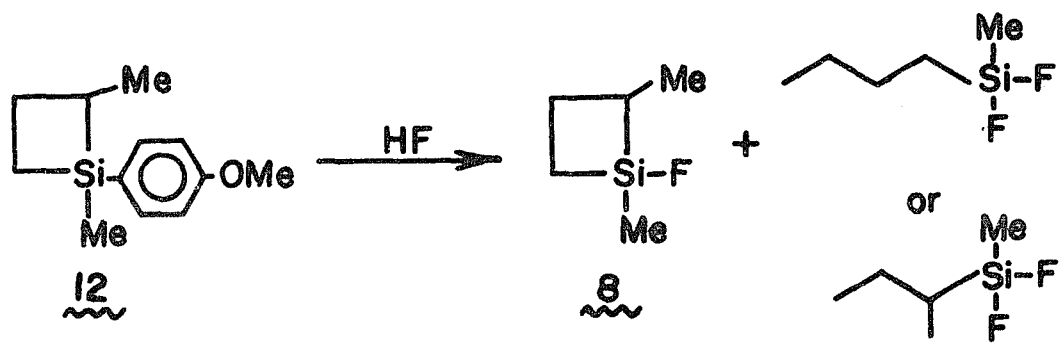
FIGURE 2-3. ^1H NMR spectra (100 MHz) of 1-(p-anisyl)-1,2-dimethyl-1-silacyclobutane. (A) 85:15 mixture of cis and trans. (B) 50:50 mixture of cis and trans. (Aromatic protons are not shown.)


A
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50


B
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50

Reaction of a 50:50 mixture of 12a and 12b with HF gave a mixture of 8 and an apparent difluorosilane (Reaction 2-9) probably

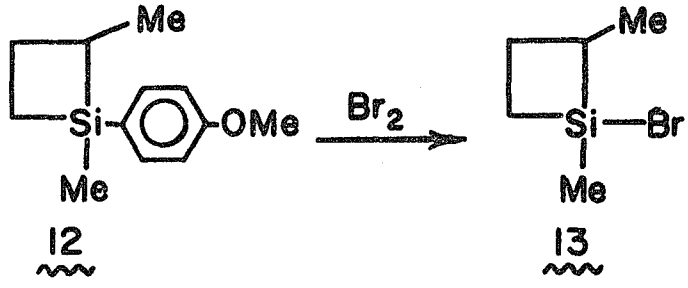
REACTION 2-9



the same as observed in the reaction of 11 with HF. The ratio of 8a to 8b was ca. 70:30 respectively. Since the same isomeric ratio of 8 was formed in both preparations, this is presumed to be an equilibrium mixture, formed possibly by fluoride ion induced isomerization of some other ratio formed in the reactions. Further evidence for this being an equilibrium ratio was the failure to observe a change in the ratio when 8 was dissolved in neat methanol. Methanol has previously been shown to equilibrate isomeric fluorosilanes.[32,58,59] That the cis isomer predominates in an equilibrium mixture of 8 is surprising in view of fact that in equilibrium mixtures of the chloro, bromo, and hydride derivatives the trans isomer predominates. Further, CNDO/2 calculations predict the trans isomer (8b) to be thermodynamically more stable.[52]

Desilylation of a 50:50 mixture of 12a and 12b with bromine in CCl_4 at ca. -23° (Reaction 2-10) afforded in high yield a 45:55

REACTION 2-10

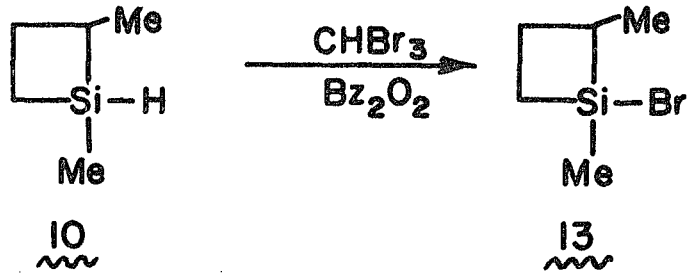


12 13

mixture of 13a and 13b respectively, the two isomers of 1-bromo-1,2-dimethyl-1-silacyclobutane. A similar isomeric ratio of 13 was formed from an 85:15 mixture of 12a and 12b. Even when the reaction mixture was analyzed immediately after reaction a 45:55 mixture was observed. Similar results have been obtained in reactions in which the anisyl group was cleaved from chiral silanes with bromine.[60] When the reaction was carried out in a diethyl ether-hexane mixture at -98° and allowed to warm up to only -78°, an 85:15 mixture of 12a and 12b gave 13a and 13b in a ratio of ca. 20:80 respectively. Similarly, a 50:50 mixture of 12a and 12b gave a 30:70 mixture of 13a and 13b respectively, which indicates the reaction was partially stereospecific.

In order to determine the stereochemistry of the reaction, 10b was brominated using bromoform and benzoyl peroxide to give a 10:90 mixture of 13a and 13b respectively (Reaction 2-11).

REACTION 2-11



10 13

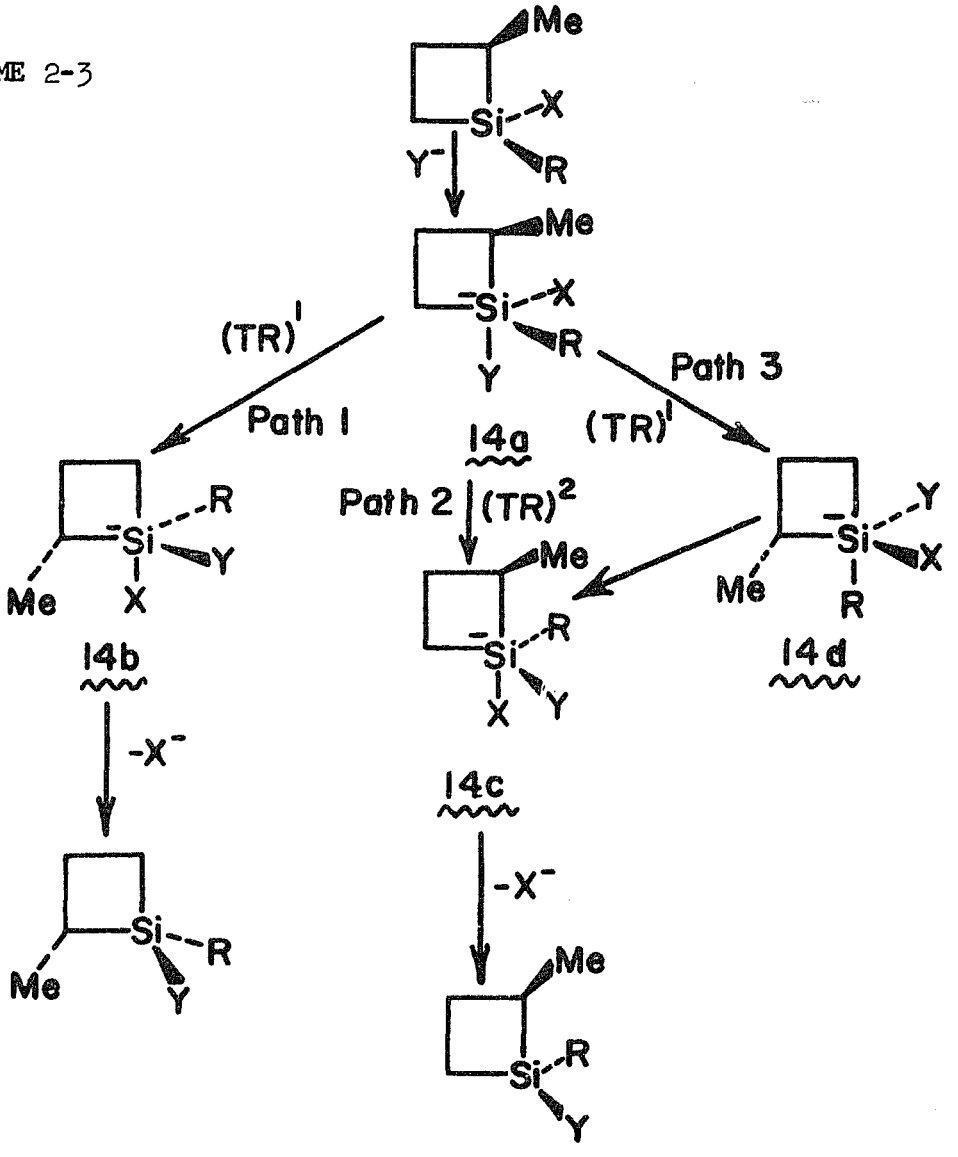
Similarily, an 80:20 mixture of 10a and 10b gave a 70:30 mixture of 13a and 13b respectively. Since the reaction occurs through a silyl radical 13b must be the trans isomer and 13a the cis isomer, indicating the preferred stereochemistry of the desilylation of 12 with bromine to be inversion of configuration.

The work presented herein shows conclusively that the reduction of 1-chloro- and 1-fluoro-1-silacyclobutanes with $LiAlH_4$, and displacement of chloride with aryl Grignard reagents occurs with predominant retention of configuration. Inversion is the normal stereochemistry of these reactions in non-strained systems. With exceptionally good leaving groups, as is found in desilylation reactions, inversion can occur in strained ring systems. A simple rationalization of these stereochemical observations is possible. "Normal" (S_N2-Si)[1,8] attack on the backside of Si (relative to the leaving group) occurs with the same stereochemical constraints as S_N2 attack on carbon; namely, the entering and leaving groups are apical and the other substituents equatorial. Attack on one of the other three faces of the approximate tetrahedron about silicon (flank attack)[61,62] leads preferentially to retention of configuration. Flank attack can be induced by coordination of the leaving group to

some portion of the entering group (S_Ni-Si)[1,9] or, as in the angle strain cases, by the inability of the substituents about Si to occupy their normal equatorial positions in the S_N2-Si transition state because of prohibitive increase in angle strain. With exceptionally good leaving groups, such as is found in desilylation reactions, this increase in angle strain is overcome and inversion of configuration is possible.

A reasonable alternative to the above explanation, and one that more satisfactorily explains the apparent inversion of configuration in the desilylation reaction, is formation of a pentacoordinate intermediate, 14a, (Scheme 2-3) which can be

SCHEME 2-3



interconverted to other pentacoordinate intermediates by turnstile rotation (TR) or Berry pseudorotation.*[63-65] A single turnstile rotation (Path 1) followed by loss of the leaving group would lead to retention of configuration whereas a double turnstile rotation (Path 2) would result in inversion of configuration. The same mechanism was postulated for the recently observed retention reaction of a cyclobutane[11] and has been applied numerous times in phosphorus chemistry.[64,66]

Why in some cases a $(TR)^1$ process is preferred and in others a $(TR)^2$ remains unknown. The answer may lie in reasoning similar to that applied to explain the nucleophilic substitution at phosphorus in a four-membered ring in which inversion of configuration was observed.[67] If R is more apicophilic than X 14d would be formed faster than 14b or 14c. The shortest route to product then is a $(TR)^1$ to give 14c followed by loss of X which would result in inversion of configuration.

Discussion of Mass Spectra.

The mass spectrum of 10 showed intense peaks at P-28 and P-36 corresponding to loss of C_2H_4 and C_3H_6 (Scheme 2-4), the

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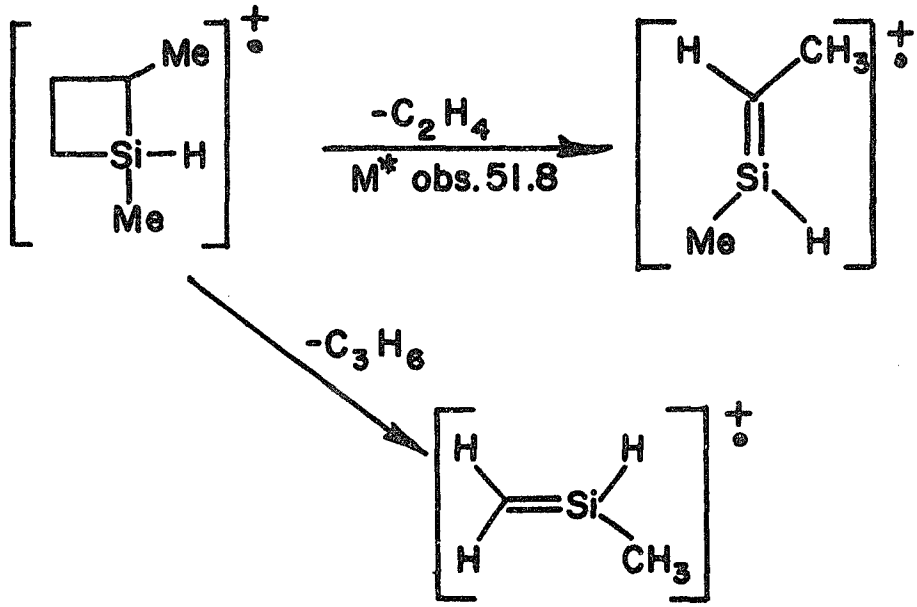
*Berry pseudorotation of a trigonal bipyramid is the increase of the angle between two equitorial substituents from 120° to 180° with the simultaneous decrease of the angle between the axial substituents from 180° to 120°. The results of a single turnstile rotation is the exchange of one axial substituent and one equitorial substituent with simultaneous rotation of the other three substituents by 120°.

SCHEME 2-4



former being the base peak. A metastable peak at 51.8 was observed that corresponded to loss of C_2H_4 from the molecular ion. Loss of C_2H_4 from silacyclobutanes has previously been observed.[68,69] All other silacyclobutane derivatives for which the mass spectra were recorded showed loss of C_2H_4 and C_3H_6 from the molecular ion also.

EXPERIMENTAL

General for All Chapters

Unless otherwise stated, all reactions were run in three-neck round bottom flasks equipped with a magnetic stirrer, reflux condenser, addition funnel, and thermometer. All glassware was flame dried and flushed with nitrogen prior to conducting the experiment under an atmosphere of nitrogen. All distillations were through a 7 cm Vigreux column unless stated otherwise. Commercial anhydrous ether was used as supplied. Pentane, quinoline, hexane, dimethylformamide (DMF), and hexamethylphosphoric triamide (HMPT) were distilled from calcium hydride. Methanol was dried over 3 Å molecular sieves; carbon tetrachloride over 4 Å molecular sieves. Where mixed solvents were used, the percent composition quoted is volume percent. Nuclear magnetic resonance (NMR) spectra were obtained routinely on a Varian A60A, equipped with a V-4343 Variable Temperature Controller, or on a Varian HA100. The solvent and standard, whether internal or external, are reported. Chemical shifts of standards were: benzene, δ 7.24; dichloromethane, δ 5.28. Infrared (IR) spectra were recorded using a Perkin Elmer 137. A Perkin Elmer Model 900 equipped with a flame ionization detector was used for routine gas-liquid partition chromatograph (glpc). Preparative glpc was carried out using a Perkin Elmer Model F-21. Glpc-mass spectra were obtained on a Perkin Elmer 990 glpc interfaced through a Biemann-Watson separator to a Hitachi-Perkin Elmer RMS-4 Mass

Spectrometer. Mass spectra were taken at 70 eV and are reported as m/e (relative abundance).

CHAPTER II

EXPERIMENTAL

(3-Chlorobutyl)dichloromethylsilane.

In a 250 ml 3-neck flask equipped as usual were placed 77.0 g (0.850 mole) of 3-chloro-1-butene and 0.10 ml of 0.20 M chloroplatinic acid hexahydrate in isopropyl alcohol. The mixture was brought to reflux and 88.3 ml (97.7 g, 0.850 mole) of dichloromethylsilane was added dropwise over a 2 hour period. After ca. 25 ml of the silane had been added the temperature rose to 65-70° and remained there during the remainder of the addition. After addition was complete the reaction mixture was held at 80-95° for 1 hour and then 70° overnight.

Distillation gave a fraction, bp 93-9°/32-3 mm., which was redistilled to give 120.5 g (69% yield) of the desired product, bp 90-7°/29-30 mm (Lit.[70] bp 182-3°). NMR[71] (CCl_4, internal TMS), δ 0.79 (s, 3H), δ 1.08 to δ 2.12 (m, 4H), δ 1.53 (d, 3H), and δ 3.92 (m, 1H).

1-Chloro-1,2-dimethyl-1-silacyclobutane, 7.

In a 1-ℓ 3-neck flask equipped as usual was placed 21.9 g (0.900 g-atom) of 40 mesh magnesium powder and 600 ml of ether. Three ml of 1,2-dibromoethane was added and the mixture refluxed for 15 min. To this activated magnesium was added dropwise 61.7 g (0.300 mole) of (3-chlorobutyl)dichloromethylsilane in 40 ml of ether over an eight hour period with refluxing. Refluxing was

continued for three days and stirring at room temperature for five days.

The reaction mixture was filtered under nitrogen and the residue washed twice with ether. The solvent was removed by rapid distillation and the remaining liquid distilled to give 25.5 g (63% yield) of 7 bp 61-5°/92-3 mm, (Lit.[24] bp 62-4°/110 mm). NMR (100 MHz) ($CDCl_3$, internal $CHCl_3$), δ 0.59 (s) and δ 0.65 (s) (total, 3H), δ 1.12 (d) and δ 1.15 (d) (total, 3H), δ 1.0 to δ 2.0 (m, 4H), and δ 2.45 (m, 1H). Relative intensities of 85:15 were observed for the singlets at δ 0.59 and δ 0.65 respectively. MS: 134(13), 119(6), 108(35), 106(100), 92(86), 78(63), 63(47) and metastables at 66.3, 64.7 and 57.3.

If the solvent was removed by slow distillation and the product distilled at 760 mm (bp 121-3°) a 75% yield was obtained of a 60:40 mixture of 7a and 7b respectively.

Keeping the reaction vessel in a cold bath at 4-6° during addition of the silane and for four days, plus seven days at 8-10° failed to increase the isomeric ratio above 85:15.

Attempted spinning band distillation of 7 at 760 mm resulted in isomerization to a 47:53 mixture of the two isomers. Spinning band distillation at 150 mm (bp 81-2°) failed to separate the isomers.

1,2-Dimethyl-1-silacyclobutane, 10

In a 250 ml 3-neck flask equipped as usual was placed 125 ml of ether and 2.30 g (0.242 g-atom of H) of crushed lithium aluminum

hydride. To this stirred mixture was added 23.1 g (0.172 mole) of a 60:40 mixture of 7a and 7b respectively in 30 ml of ether at a rate sufficient to maintain refluxing. Refluxing was continued 1/2-hour after addition was complete.

After filtering, the reaction mixture was added to 150 ml of ice water containing 30 g of ammonium chloride. The ether layer was washed once with 1 M aqueous ammonium chloride, twice with water, and dried over magnesium sulfate. Distillation gave 10.1 g (59% yield) of 10, bp 84-7° (Lit.[25] bp 85-7°/748 mm).

Analysis by glpc using a 16 ft. x 1/8 in. column of 15% Apiezon L on 60-80 mesh Chromosorb W at 85° showed an impurity, 10%, retention time of 4.2 min, and the two isomers, 10b and 10a, retention times of 4.7 and 5.3 min, 37% and 53% respectively (10a:10b ratio of 59:41). Similarily, reduction of a 78:22 mixture of 7a and 7b gave an 80:20 mixture of 10a and 10b as determined by glpc analysis of the reaction mixture.

The isomers were separated by preparative glpc on a 5'4" x 3/4" column of 10% Apiezon L on 60-80 mesh Chromosorb W operating at a temperature of 85° with a nitrogen flow rate of 270 ml/min. The trans- and cis-isomers had retention times of 6.4 and 7.2 minutes respectively. Attempted spinning band distillation of 10 resulted in polymerization. NMR (100 MHz) ($CDCl_3$, internal TMS) 10a: 0.28 (d, J =4Hz, 3H), δ 1.05 (d, 3H), δ 0.76 to δ 1.95 (m, 4H), δ 2.45 (m, 1H), and δ 4.75 (m, 1H); 10b: 0.32 (d, J = 4Hz, 3H), δ 1.11 (d, 3H), δ 0.58 to δ 1.87 (m, 4H), δ 2.40 (m, 1H), and δ 4.42 (m, 1H): IR (film): 2900 s, 2100 s, 1450 m, 1400 w, 1250 s, 1180 w, 1130 m,

1060 m, 970 m, 920 s, 890 s, 855 s, and 730 s; mass spectrum: 100(10), 85(14), 72(100), 58(45), 43(45) and a metastable at 51.8.

Stereospecific Preparation of 1-Chloro-1,2-dimethyl-1-silacyclobutane from 1,2-Dimethyl-1-silacyclobutane.

In a 25 ml one-neck flask equipped with a condenser was placed 2.16 g (21.6 mmole) of 95% isomerically pure 10a, 17 ml (175 mmole) of dry carbon tetrachloride and 0.05 g of benzoyl peroxide. The mixture was held at 80° for 1 hour, an additional 0.05 g of benzoyl peroxide added and the mixture heated at 80° 1 hour longer. Analysis of the reaction mixture by NMR showed a 94:6 ratio of 7a and 7b.

Distillation gave 1.63 g (56% yield) of 94% isomerically pure 7a, bp 59-61°/89-90 mm.

Similarly, reaction of 0.78 g of 98% 10b, 1.0 ml of carbon tetrachloride, and 0.02 g of benzoyl peroxide in an NMR tube at 80° for 1 hour gave >95% pure 7b, as determined by NMR analysis of the reaction mixture.

1,2-Dimethyl-1-methoxy-1-silacyclobutane, 9.

To 3.34 ml (82.8 mmole) of methanol and 10.1 ml (82.8 mmole) of quinoline in 60 ml of ether was added dropwise 11.12 g (82.8 mmole) of a 70:30 mixture of 7a and 7b in 10 ml of ether. After stirring 4 hours the mixture was filtered and distilled to give 4.15 g (38% yield) of 9, bp 115-9° (Lit.[24] bp 75-7°/ 135 mm). NMR[24] (CCl_4, internal benzene): δ 0.10 (s) and δ 0.15 (s) (total 3H),

δ 0.80 to δ 2.30 (m, 8H), δ 3.40 (s), and δ 3.48 (s) (total 3H). Relative intensities of 70:30 were observed for singlets at δ 0.10 and δ 0.15 respectively, and 70:30 for singlets at δ 3.40 and 3.48 respectively. IR (film) 2900 s, 1460 m, 1420 w, 1250 s, 1190 m, 1130 m, 1100 s, 970 m, 920 m, 880 m, 850 m, 830 s, 800 s, and 755 s.

Reduction of 1,2-Dimethyl-1-methoxy-1-silacyclobutane.

In an 8 ml vial were placed 6.5 mg (0.73 mg-atoms of H) of $LiAlH_4$ and 2.0 ml of ether. Through a septum 52. mg (0.40 mmole) of a 70:30 mixture of 9a and 9b was added via syringe and the mixture stirred 1/2 hour. Glpc-mass spectrometry analysis showed 10a and 10b were formed in a 75:25 ratio.

1,2-Dimethyl-1-fluoro-1-silacyclobutane, 8.

In a 50 ml 1-neck flask were placed 15.33 g (114 mmole) of a 70:30 mixture of 7a and 7b respectively and 9.0 g (87 mmole) of anhydrous zinc fluoride. The flask was equipped with a magnetic stirrer and set for distillation. Distillation gave a fraction, bp 85-112°, which was combined with 9.0 g (87 mmole) of fresh zinc fluoride and redistilled, the fraction bp 80-85° being collected. Redistillation of this fraction from 1.0 g of fresh zinc fluoride gave 9.21 g (68% yield) of 8, bp 83-4°. NMR (CCl_4, internal benzene); δ 0.25 (d, J = 8 Hz) and δ 0.32 (d, J = 8 Hz) (total of 3H), δ 1.05 (m, 3H), and δ 0.83 to 2.25 (m, 5H); estimated relative intensities were 70:30 for doublets at δ 0.25 and δ 0.32 respectively. ^{19}F NMR

($CFCl_3$, solvent as reference) δ 137.6 (m) and δ 154.7 (m) (relative intensities of 75:25 respectively); MS: 118(7), 103(6), 90(94), 77(77), 76(100), 63(50), 62(92), 47(83), and metastables at 42.8 and 50.2; Anal. calc'd for $C_5H_{11}FSi$: C, 50.79; H, 9.38; Si, 23.78. Found: C, 50.59; H, 9.40; Si, 23.60.

A similar preparation using a 50:50 mixture of 7a and 7b gave a 70:30 mixture of 8a and 8b as determined by NMR.

Reduction of 1,2-Dimethyl-1-fluoro-1-silacyclobutane.

In an 8 ml vial equipped with a magnetic stirrer were placed 45.6 mg (4.94 mg-atoms of H) of $LiAlH_4$ and 5. ml of ether. After equipping with a septum 0.50 g (4.2 mmole) of a 70:30 mixture of 8a and 8b was added *via* syringe and the mixture stirred 15 min. Glpc-mass spectrometry analysis showed 10a and 10b were formed in a 68:32 ratio.

1,2-Dimethyl-1-(*p*-tolyl)-1-silacyclobutane, 11.

To 30.0 g (0.223 mole) of a 50:50 mixture of 7a and 7b in 100 ml of ether was added dropwise a solution of *p*-tolylmagnesium bromide prepared from 42.0 g (0.245 mole) of 4-bromotoluene and 8.0 g (0.33 mole) of magnesium turnings in 400 ml of ether. After stirring under reflux for 1 hour the mixture was hydrolyzed by addition to 35 g of ammonium chloride in 500 ml of ice water. The ether layer was washed once with water and dried over magnesium sulfate. After removing the solvent, the remaining liquid was distilled to yield 29.0 g (68% yield) of a 50:50 mixture of 11a and

11b, bp 73-5°/1.0 mm. NMR (CH_2Cl_2, solvent as reference) δ 0.50 (s) and δ 0.52 (s) (total, 3H) (ca. 50:50), δ 0.98 (d, J = 7 Hz) and δ 1.14 (d, J = 7 Hz) (total, 3H), δ 0.95 to δ 1.93 (m, 4H), δ 2.37 (broad s, 3H), δ 2.31 to δ 2.61 (m, 1H) δ 7.24 (m, 2H) and 7.56 (m, 2H); IR (film): 2900 s, 1600 m, 1450 m, 1400 w, 1250 s, 1180 w, 1130 m, 1110 s, 970 m, 920 w, 870 m, 850 s, and 780 s; Mass spectrum: 190(16), 175(1), 162(45), 148(100), 135(67), 134(45), 133(73), 131(22), 119(59), 105(20), 93(20), and metastables at 138.1 and 110.8. Anal. calc'd: C, 75.71; H, 9.53; Si, 14.76. Found: C, 75.52; H, 9.43; Si, 15.00.

Reaction of 11 with HF.

In a dry polyethylene test tube equipped with a polyethylene stopper was placed via syringe 1.7 g of 11. Anhydrous HF was bubbled through 11 for 3 hours by use of a stainless steel needle. After standing overnight nitrogen was bubbled through the solution for 1 hour. The reaction mixture was analyzed directly. NMR (CCl_4, external TMS), δ 0.28 (t), δ 0.60 to 1.80 (m), δ 2.31 (s), and δ 7.10 (s), the latter two chemical shifts characteristic of toluene; MS: parent mass 138. The product probably was sec-butyl- and/or n-butyldifluoromethylsilane.

A similar reaction was stopped before all starting material was consumed. NMR analysis showed no 8 was present.

Reaction of 11 with Bromine.

To 4.40 g (23.2 mmole) of 11 in 10 ml of CCl_4 held in an ice bath was added 3.7 g (23.2 mmole) of bromine in 10 ml of CCl_4. After addition was completed the solvent was removed by distillation under reduced pressure and the product distilled to give 4.5 g (55% yield) of a clear liquid tenatively identified as a 2:1 mixture of bromo (3-bromobutyl)methyl(p-tolyl)silane and bromo (3-bromo-1-methylpropyl)methyl(p-tolyl)silane, bp 105-135°/0.9 mm. NMR (CCl_4, internal TMS) δ 0.76 (s), δ 0.87 to δ 2.10 (m), δ 1.66 (d), δ 2.33 (s), δ 3.38 (m), δ 4.20 (m), δ 7.12 (d), and δ 7.46 (d).

1,2-Dimethyl-1-(4-methoxyphenyl)-1-silacyclobutane, 12.

To a solution of 26.9 g (0.200 mole) of a 50:50 mixture of 7a and 7b in 100 ml of ether was added with stirring the top layer of a solution of 4-methoxyphenylmagnesium bromide obtained from 39.0 g (0.208 mole) of p-bromoanisole and 7.0 g (0.287 mole) of magnesium turnings in 350 ml of ether. The lower layer was then added dropwise and the mixture stirred 2 hours under reflux.

The reaction mixture was hydrolyzed in 300 ml of ice water containing 20 g of ammonium chloride. The ether layer was washed once with water and dried over magnesium sulfate. After removing the solvent, the remaining liquid was distilled, the fraction bp 80-6°/0.5 mm was collected and redistilled to give 26.7 g (65% yield) of a 50:50 mixture of 12a and 12b, bp 72-6°/0.3 mm. NMR (CH_2Cl_2, solvent as reference)(100 MHz) δ 0.55 (s) and δ 0.57 (s) (total 3H) (ca. 50:50), δ 1.03 (d, J = 7 Hz) and δ 1.18 (d, J = 7 Hz) (total 3H),

δ 0.94 to δ 2.00 (m, 4H), δ 2.55 (m, 1H), δ 3.82 (s), and δ 3.83 (s), (total 3H), δ 6.99 (m, 2H), and δ 7.59 (m, 2H); IR (film): 2900 s, 1600 s, 1480 s, 1270 s, 1240 s, 1180 m, 1130 w, 1110 s, 1140 m, 965 w, 915 w, 870 w, 850 m, and 780 m; mass spectrum: 206(14), 191(2), 178(32), 164(100), 151(61), 135(37), 134(38), 121(22), 119(19), and metastable at 109.5; Anal. calc'd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79; Si, 13.61. Found: C, 69.91; H, 8.90; Si, 13.74.

Similarly, reaction of 4-methoxyphenylmagnesium bromide with an 85:15 mixture of 7a and 7b respectively gave an 75% yield an 85:15 mixture of 12a and 12b respectively.

Reaction of 12 with HF.

In a dry polyethylene test tube equipped with a polyethylene stopper was placed 5.8 g of a 50:50 mixture of 12a and 12b. Anhydrous HF was bubbled through the neat compound for 2 hours followed by nitrogen for 1 hour. Distillation gave a fraction 0.91 g, bp 78-83°, the NMR spectrum of which showed chemical shifts characteristic of 8a and 8b (ca. 70:30 respectively) and approximately an equal amount of the product obtained from reaction of 11 with HF.

1-Bromo-1,2-dimethyl-1-silacyclobutane, 13.

In a one-neck 100 ml flask equipped with a magnetic stirrer and addition funnel was placed 10.4 g (50.5 mmole) of a 50:50 mixture of 12a and 12b and 20 ml of carbon tetrachloride. Bromine (8.10 g, 50.5 mmole) in 15 ml of carbon tetrachloride was added dropwise with stirring while keeping the flask in a dry ice-acetone bath at -50 to

-55°. Distillation gave 7.50 g (83% yield) of a 50:50 mixture of 13a and 13b, bp 70-1°/68 mm. NMR (CCl_4, internal benzene); δ 0.67 (s) and δ 0.73 (s) (total 3H) (50:50), δ 1.06 (d, 3H), and δ 0.97 to δ 2.78 (m, 5H); mass spectrum: 180(15), 178(16), 165(6), 163(6), 152(100), 150(100), 138(89), 136(89), 124(66), 122(66), 109(56), 107 (55), 99(8), 90(68), 76(66), and 62(57). Anal. calc'd for $C_5H_{11}BrSi$: C, 33.52; H, 6.19; Si, 15.69. Found: C, 33.64; H, 6.25; Si, 15.55. Similarly, an 85:15 mixture of 12a and 12b led to a 64% yield of a 45:55 mixture of 13a and 13b respectively.

Reaction of 12 with Bromine at -98°.

In a 100 ml three-neck flask equipped with a mechanical stirrer, addition funnel and thermometer were placed 5.48 g (26.6 mmole) of an 85:15 mixture of 12a and 12b and 50 ml of ether. The flask was placed in a methanol-liquid nitrogen slurry (-98°) and 4.25 g (26.6 mmole) of bromine in 10 ml of dry hexane was added dropwise over a 1 hour period. The mixture was stirred 2 hours as it warmed slowly to -78°. Analysis by NMR showed only a trace of starting material present and that 13a and 13b were formed in ca. a 20:80 ratio. Similarly, a 50:50 mixture of 12a and 12b gave a 30:70 ratio of 13a and 13b.

Stereospecific Preparation of 13 from 10.

Reaction of 78 mg of 98% pure 10b with 1.0 ml of $CHBr_3$ and 20 mg of benzoyl peroxide at 80° for 15 min. gave a 10:90 mixture of 13a and 13b as determined by NMR. Similarily an 80:20 mixture of 10a and 10b gave a 70:30 mixture of 13a and 13b.

CHAPTER III

SOLVOLYSIS OF 1,2-DIMETHYL-1-SILACYCLOBUTANE

One reaction in which the presence of an extracoordinate intermediate has been proposed is base-catalyzed hydrolysis of triorganosilicon hydrides.[61,72] The normal products of the reaction in aqueous alcohol are the silanol, 14, the alkoxide, 15, and hydrogen (Reaction 3-1). The silanol normally loses water to form

REACTION 3-1

$$R_3SiH \xrightarrow{OH^-, R'OH, H_2O} \underset{14}{R_3SiOH} + \underset{15}{R_3SiOR'} + H_2$$

the disiloxane, 16 (Reaction 3-2). The rate of the reaction is

REACTION 3-2

$$2R_3SiOH \xrightarrow{-H_2O} \underset{16}{(R_3Si)_2O}$$

first-order in both silane and base.[74] That the Si-H bond is broken in the rate-determining step has been shown by the observation of isotope effects. For isotopic substitution in the silicon hydride small kinetic isotope effects, $k_H/k_D < 1.5$, were observed.[75-79] A kinetic isotope effect of 1.97 has been observed using solvent substituted with deuterium,[78] and solvent product isotope effects

have been shown to vary from 2 to 6.[72,73] The isotope effects have been interpreted in terms of a non-linear transition state which caused the observed values to be less than the theoretical value of 4.[72,79]

These observations are in accord with two main mechanistic choices, either a concerted process (Reaction 3-3), which is probably a

REACTION 3-3

$$OH^- + R_3SiH + H_2O \rightarrow HOSiR_3 + H_2 + OH^-$$

S_Ni-Si mechanism, or a two-step process (Reaction 3-4) with rapid

REACTION 3-4

$$OH^- + R_3SiH \rightleftarrows [HOSiR_3H]^- \qquad (a)$$

$$\underset{\sim}{17}$$

$$[HOSiR_3H]^- + H_2O \rightarrow HOSiR_3 + H_2 + OH^- \qquad (b)$$

and reversible formation of a pentacoordinate silicon intermediate $\underset{\sim}{17}$, followed by slow rate-determining loss of hydride that is concerted with hydrogen formation. Preference for the latter choice is found in the fact that substantial charge development at silicon occurs, as shown by the observation of Hammett ρ values of +2 to +5.[81-87] This can be interpreted to mean that the nucleophile must bind tightly to silicon in order to effect displacement. The greatly increased reactivity of strained bridgehead silanes and silacyclobutanes, relative to acyclic silanes, has also been

suggested as evidence for a pentacoordinate intermediate,[7,55] since these systems have C-Si-C angles close to 90°, the angle required between axial and equatorial substituents in trigonal bipyramids. A similar argument has been used to explain the increased reactivity observed in small ring phosphorus compounds over comparable acyclic systems.[90]

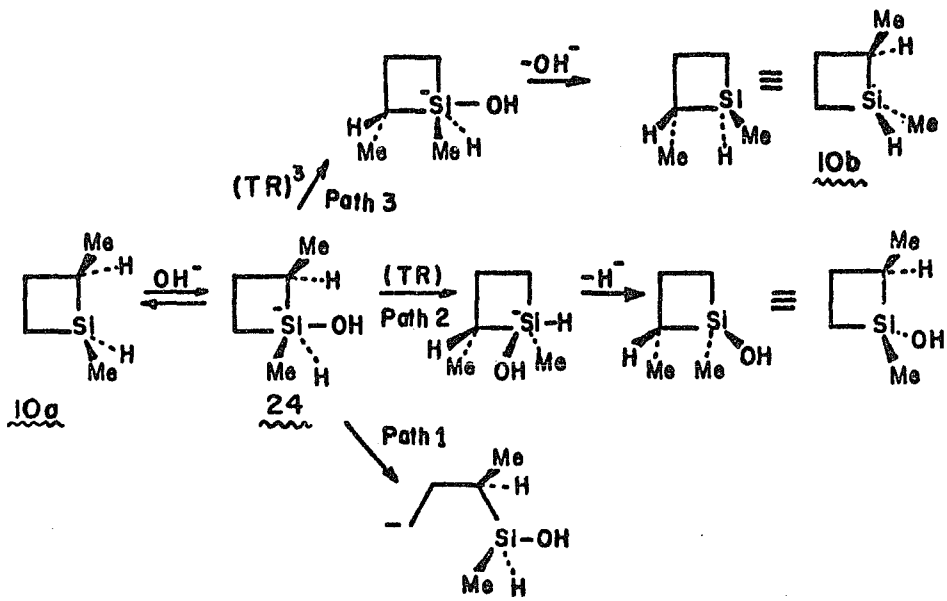
The stereochemistry of hydrolysis of silicon hydrides appears to be predominant retention of configuration although, in the polar solvent methanol, racemization occurred.[10] Regardless, this allows no distinction of the mechanism since both inversion and retention of configuration are reasonable possibilities for both mechanisms.

Nucleophilic displacements at tetracoordinate phosphorus frequently do proceed through pentacoordinate intermediates which have sufficient lifetimes to undergo pseudorotations, and stereochemical results are predictable in terms of the relative stabilities of stereoisomeric trigonal bipyramids.[63-66] The two pathways that have been proposed to operate for pseudorotation are Berry pseudorotation (BPR) and turnstile rotation (TR).[65] The results of both are equivalent.

If pentacoordinate intermediates are formed in the solvolysis of silicon hydrides and if pseudorotations are occurring, predictable results should be obtainable. The system in which pseudorotation would most likely occur, if it is ever going to be important in displacement reactions with organosilanes, is the silacyclobutane system since ring strain should favor formation of the trigonal bipyramidal intermediate. Base-catalyzed hydrolysis of <u>cis</u>- and

trans-1,2-dimethyl-1-silacyclobutane, 10a and 10b respectively, allows studies to be made which were not previously possible. If in the course of hydrolysis of 10a, a pentacoordinate intermediate is formed following the same groundrules which seem to apply for phosphorus compounds[63,66] (axial entry of hydroxide to form a trigonal bipyramid with one ring bond axial), then several eventual outcomes are possible, including those outlined in Scheme 3-1. It

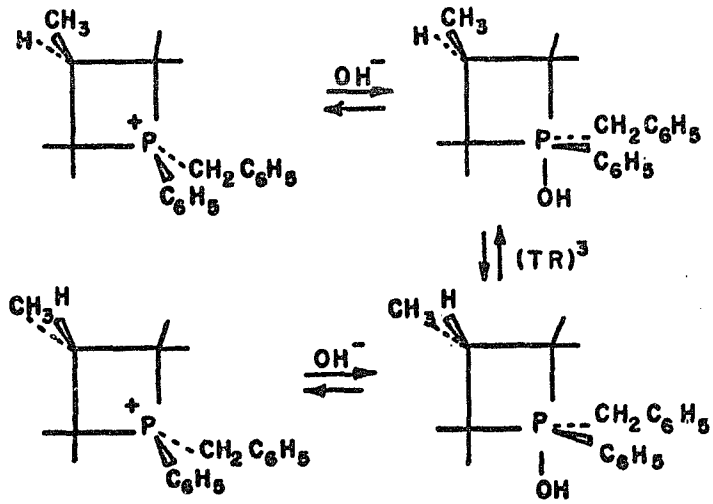
SCHEME 3-1



seemed of paramount interest to determine whether Path 3 of Scheme 3-1 were operating, since cis-trans isomerization would require the intervention of an extracoordinate species with sufficient lifetime to undergo pseudorotations. It is possible that 10a could be converted to 10b by ring opening to a carbanion followed by reclosure, but that is a highly unlikely process in a protic solvent

mixture. A closely related case, in which isomerization of a four-membered phosphorus ring occured with base catalysis, was also proposed to result from formation of a trigonal bipyramid which underwent pseudorotation[89] (Scheme 3-2). Pseudorotation has been

SCHEME 3-2



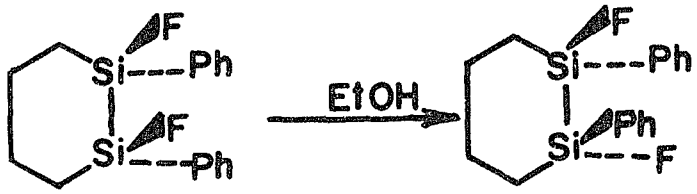
proposed to occur at silicon in the alcohol catalyzed racemization of an optically active fluorosilane[58,59] (Reactic 3-5) and in the

REACTION 3-5

$$(+)\text{NpPhMeSiF} \xrightarrow{\text{MeOH}} (\pm)\text{NpPhMeSiF}$$

isomerization, again catalyzed by alcohol, of a 1,2-difluoro-1,2-disilacyclohexane[32] (Reaction 3-6). Both reactions were believed

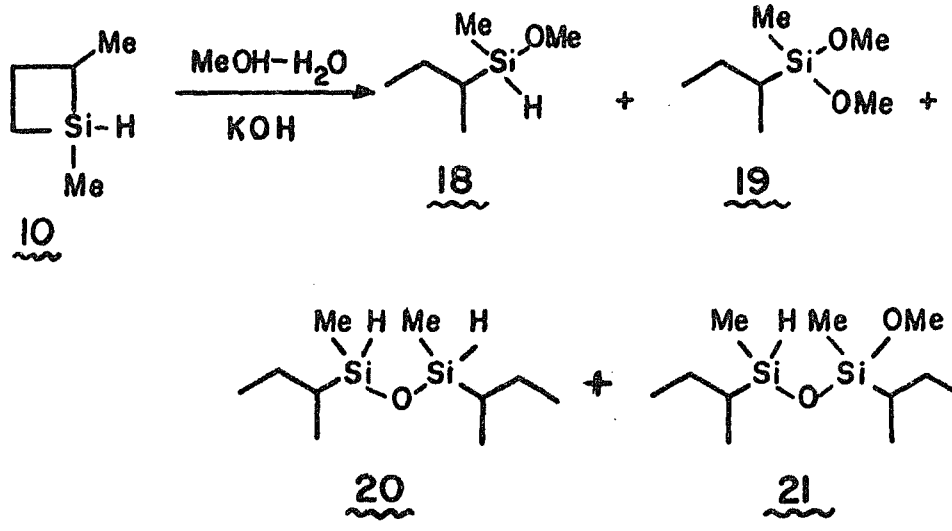
REACTION 3-6



to occur by BPR or TR of a pentacoordinate species formed by methoxide attack at Si, followed by loss of methoxide. Sommer suggested that in general pentacoordinate intermediates are uncommon for reactions of triorganosilanes, the fluoride derivatives being a special case.[1]

The reaction of 10a with 95% (by volume) methanol-water catalyzed by hydroxide ion was complex. At least nine products were formed, but when relatively short reaction times were used (ca. two half-lives) four of the products accounted for greater than 75% of the product mixture. Three of the products shown in Reaction 3-7,

REACTION 3-7



sec-butylmethylmethoxysilane, 18, sec-butylmethyldimethoxysilane, 19, and 1,3-di(sec-butyl)-1,3-dimethyldisiloxane, 20, were identified by comparison of glpc retention times and mass spectra with those of authentic samples prepared as described in the experimental part. The fourth product, 1,3-di(sec-butyl)-1,3-dimethyl-1-methoxydisiloxane, 21, was identified after isolation from the product mixture by thick layer chromatography. All of the products isolated are ring-opened ones, and, not surprisingly, the ring opens in only one direction forming the more stable primary carbanion to give sec-butylsilanes and not n-butylsilanes. An authentic sample of 1,3-dibutyl-1,3-dimethyldisiloxane, 22, was prepared and shown not to be the same as any of the hydrolysis products by comparison of glpc retention times and mass spectra.

No products containing the silacyclobutane ring intact were isolated, but using an argument previously formulated,[7] the presence of either or both 1-hydroxy- and 1-methoxy-1,2-dimethyl-1-silacyclobutane which underwent subsequent rapid ring opening, was inferred. Rates of hydrogen evolution for 10a and 10b and for the hydride-containing products, 18 and 20, are given in Table 3-1. When 10a and 10b were hydrolyzed there was an initial period of rapid hydrogen evolution up to approximately 30% reaction, followed by continued but much slower evolution. The only reasonable explanation for this phenomenon was that during the initial period hydride displacement from 10 and ring opening of 10 were competing, and thereafter slow hydride displacement from the ring-opened products occurred. Indeed, both 18 and 20 evolved hydrogen at a rate that was slower by a factor

TABLE 3-1

Rates of Hydrogen Evolution at 0°

Compound	[KOH] M	$10^3 \times k'$[a] sec^{-1}	k M^{-1} sec^{-1}	k_{rel}	H_2 evolved, % of theoretical
10a	1.5×10^{-4}	13.5	90	1.6×10^4	47
10b	1.5×10^{-4}	5.71	38	6.9×10^3	26
18	0.201	5.36	2.7×10^{-2}	4.9	100
20	0.815	4.48	5.5×10^{-3}	1	100

[a] Pseudo-first-order rate constants.

of at least 10^3 compared to the initial rate from 10. In addition to the kinetic evidence, glpc-mass spectral analysis of the product mixture afforded reasonably good evidence that one of the solvolysis products was 1-(sec-butylmethylsiloxy)-1,2-dimethylsilacyclobutane, 23. This product was present at early stages of the reaction but then disappeared as additional 21 was formed. The mass spectrum of this product is discussed in a later section.

Slight deviation from linearity in the pseudo-first-order plots were observed, probably from formation of silanol anions.[90] Salt effects were not taken into account since they would have little influence on relative rates.[74,90] Further, it was more difficult to obtain pure samples of the trans silacyclobutane isomer, 10b, so that kinetic runs had to be made on small amounts of sample with consequent greater uncertainty. However, without question the cis isomer, 10a, gave hydride displacement at a rate about twice that of

the trans isomer, 10b. It seems most reasonable to attribute the rate differential to a steric acceleration. If formation of the intermediate, 24, (Scheme 3-1) from 10a is the rate determining step, then it is easy to imagine some relief of steric interactions between the cis methyl groups which would accelerate the formation of 24 relative to the corresponding intermediate from 10b. Of course, arguments of a similar nature could be advance based on the assumption of a direct displacement mechanism (S_Ni-Si[1] or S_N2-Si Retention[33]).

Reaction of the cis isomer, 10a, at 0° for approximately two half-lives (based on the initial rapid rate of hydrogen evolution) was followed by quenching with excess HCl. No isomerization of 10a to 10b was detected by glpc. Control experiments indicated that the method used could have detected as little as 0.5% isomerization. That isomerization fails to occur under these conditions does not, of course, rule out the possibility of an extracoordinate intermediate. A pentacoordinate species could be formed in the rate-determining step as inferred by Sommer from determination of isotope effects on the reactivity of 1-methyl-1-silacyclobutane.[78] This is inconsistent however, with other isotope effects observed for acyclic systems, and, as previously discussed, certainly the silacyclobutane ring system ought to react through rapid reversible formation of a pentacoordinate intermediate if acyclic systems do.

An intermediate could be formed rapidly and reversibly but with the condition that Path 3 in Scheme 3-1 is considerably slower than Paths 1 and 2. This would not be surprising since $(TR)^3$ processes

tend to have higher activation energy barriers than a single TR process.[66]

The lack of observation of isomerization and the observed cis/trans rate ratio seem to be more in agreement with slow formation of a pentacoordinate intermediate or direct S_Ni-Si displacement, evidence for the latter being the observed kinetic isotope effects. It is indeed quite possible that unstrained systems react by direct displacement while strained ones react through rate-determining intermediate formation.

Since the formation of hydrogen appears to be concerted, hydrolysis of silanes in aprotic solvents should occur at greatly reduced rates. Thus, if an intermediate were formed the possibility of isomerization would be enhanced. Acting under this assumption, other media were explored. During the course of this study, slow isomerization of 10a was observed in dimethylformamide (DMF) alone. Further studies revealed that the actual reagent causing isomerization was cyanide ion which has previously been shown to be an impurity in DMF, generated by light.[91,92] This was demonstrated by using DMF distilled from calcium hydride in the dark. No isomerization was observed for periods up to one week when the reaction mixture was kept in the dark, and as expected, rapid isomerization occurred when potassium cyanide was added.

Attempts were made to determine the order of the reaction in cyanide ion by determining pseudo-first-order rate constants, k_1, at various KCN concentrations, as described in the experimental section. A plot of log[KCN] vs. log k_1 (Equation 3-1) should have given a

EQUATION 3-1

$$\log k_1 = x \log[KCN] + \log k_3$$

straight line of slope x, the order of the reaction in KCN. Irreproducible results were observed in determining pseudo-first-order rate constants (Table 3-2), although individual runs gave good

TABLE 3-2

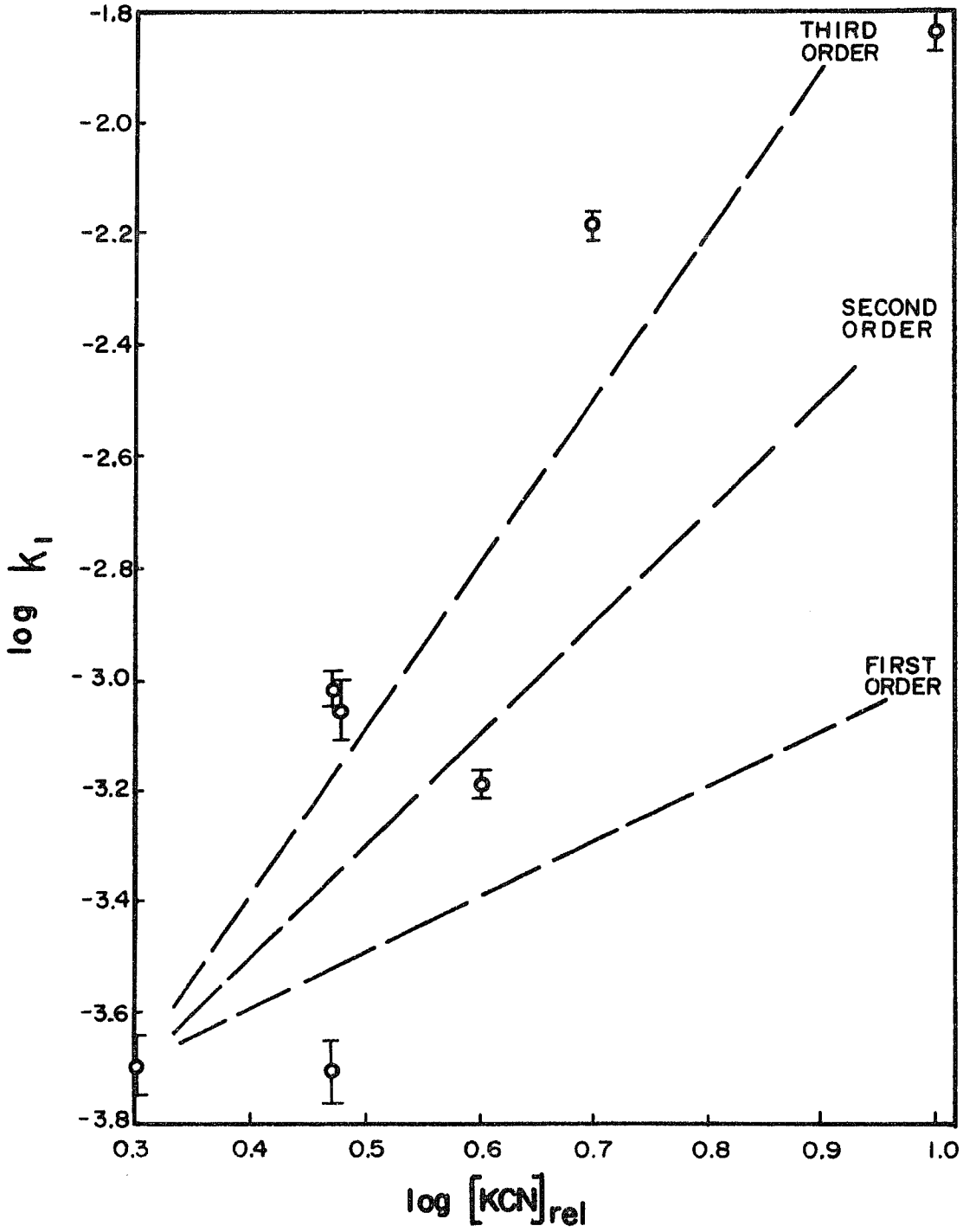
Pseudo-first-order Rate Constants for Isomerization of 10a

[KCN] (relative)	$10^4 k_1$ (min^{-1})
10	150. ± 10.
5	66. ± 2.
4	6.4 ± 0.2
3	9.5 ± 0.9
3	8.68 ± 1.
3	1.94 ± .2
2	2.0 ± 0.2

straight lines. Thus, the plot of log k_1 vs. log[KCN] (Figure 3-1) failed to reveal the order of the reaction.

The origin of the variable results was unknown but may have been due to autoionization of traces of water which could have caused substantial changes in the cyanide ion concentrations (Reaction 3-8), since low concentrations of potassium cyanide were

FIGURE 3-1. Plot of log k_1 vs. log$[KCN]_{rel}$ for isomerization of <u>cis</u>-1,2-dimethyl-1-silacyclobutane in DMF.


-1.8
-2.0
-2.2
-2.4
-2.6
-2.8
-3.0
-3.2
-3.4
-3.6
-3.8
log k_1
THIRD ORDER
SECOND ORDER
FIRST ORDER
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
log $[KCN]_{rel}$

REACTION 3-8

$$H_2O + CN^- \rightleftarrows OH^- + HCN$$

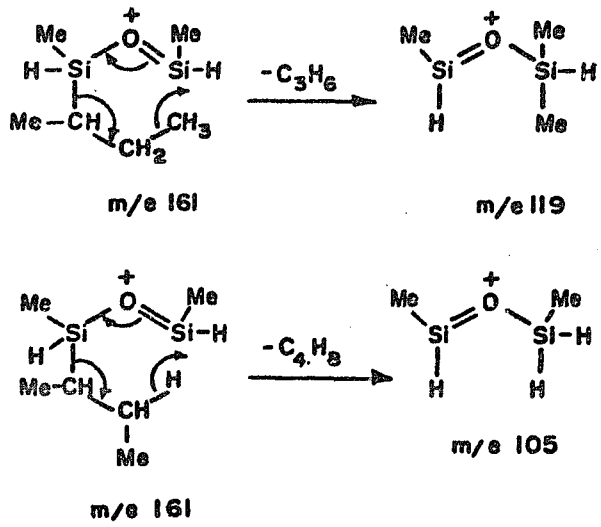
necessary to have a sufficiently slow reaction rate to measure by the method used.

That isomerization occurred does not indicate the presence of an extracoordinate intermediate, since ring opening to a carbanion, which would not undergo further reaction in anhydrous DMF, followed by reclosure could have resulted in isomerization.

Discussion of Mass Spectra.

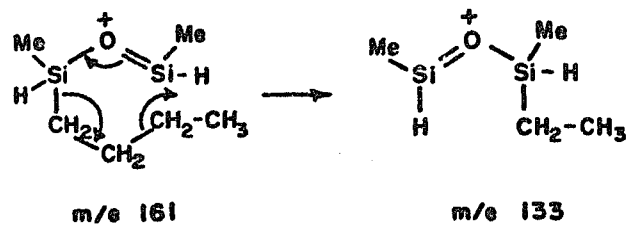
Significant differences in the mass spectra of the sec-butyl and n-butyl analogs, 20 and 22, were observed. Both showed an intense peak at mass 161 formed by loss of C_4H_9 from the parent. Loss of C_3H_6 from mass 161 leading to a fragment of mass 119 is observed only for 20. A metastable ion at mass 88.0 provided evidence in support of this pathway. However, both 20 and 22 showed loss of C_4H_8 from mass 161 leading to a mass of 105, the base peak for both compounds. This was supported by a metastable ion at mass 68.5 in the spectrum of 20. An acceptable six-membered ring transition state can be written for both rearrangements (Scheme 3-3). This sort of transition state was supported by a more intense

SCHEME 3-3



mass of 133 in 22 than in 20, presumably due to loss of C_2H_4 from mass 161 by a similar transition state (Scheme 3-4) although no

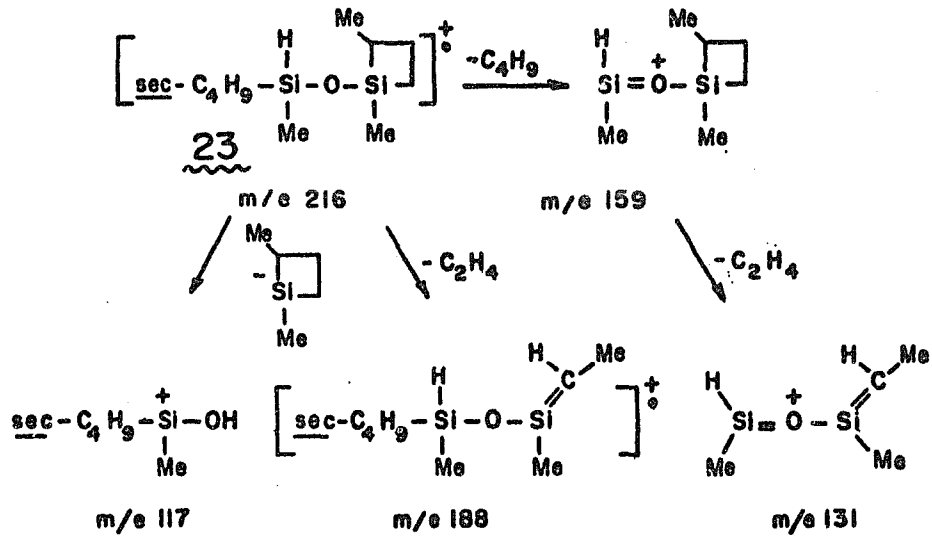
SCHEME 3-4



metastable ion was observed to support this. There has been no report of direct analogs of these rearrangements in organosilanes, although numerous reports of silyl-McLafferty-type rearrangements have appeared,[93-95] and it has been noted[96] that rearrangement of atoms or groups to the silicon atoms of siliconium ions is a generally favorable process.

The fragmentation pattern of the transient product, 23, shown in Scheme 3-5, provided ample evidence for the suggested

SCHEME 3-5



structure. The parent ion, mass 216, showed loss of CH_3 leading to mass 201 and loss of C_4H_9 leading to mass 159, the base peak. The presence of two Si atoms in mass 159 was confirmed by the relative intensities of masses 160 and 161. The presence of the silacyclobutane ring was indicated both by loss of C_2H_4 from the parent ion leading to mass 188 and from mass 159 to give mass 131. The latter was supported by a metastable peak at mass 108. No cleavage of a silicon-oxygen bond was observed in the disiloxanes, 20 or 22. However, 23 showed loss of $C_5H_{11}Si$ leading to mass 117.

CHAPTER III

EXPERIMENTAL

Methyltrimethoxysilane.

Methyltrimethoxysilane was prepared as previously reported[97] and obtained in 66% yield, bp 98-101° (Lit.[97] bp 102°); NMR (CCl_4, external TMS): δ 0.00 (s, 3H) and δ 3.45 (s, 9H).

1,3-Dibutyl-1,3-dimethyldisiloxane, 22.

By the method of Liu,[98,99] 1,3-dibutyl-1,3-dimethyldisiloxane was prepared in 18% yield, bp 77-8°/9-10 mm (Lit.[98] bp 99-100°/22 mm; NMR (CCl_4, external TMS): δ 0.10 (d, 6H), δ 3.50 to δ 1.62 (m, 18H), and δ 4.52 (m, 2H); IR (film): 2900 s, 2100 s, 1450 m, 1400 m, 1360 m, 1330 w, 1300 w, 1250 s, 1180 m, 1060 s, 960 m, 870 s, and 750 s; mass spectrum: 218(3), 216(11), 161(70), 159(14), 147(17), 133(2), 119(3), 105(100), 103(9), 91(15), and metastable at 68.5; Anal. calc'd for $C_{10}H_{26}OSi_2$: C, 54.94; H, 11.99; Si, 25.71. Found: C, 54.84; H, 11.95; Si, 25.66.

sec-Butylmethylchlorosilane.

To a solution of 26.0 g (0.226 mole) of methyldichlorosilane in 50 ml of dry ether was added with stirring a solution of sec-butylmagnesium bromide obtained from 27.4 g (0.200 mole) of 2-bromobutane and 7.0 g (0.29 g-atom) of magnesium powder in 320 ml of dry ether. After stirring 20 h under reflux the mixture was filtered under nitrogen, the residue washed once with dry ether and

the filtrate distilled to yield 12.7 g (47% yield) of the desired product, bp 119-125°; NMR (CCl_4, external TMS): δ 0.39 (d, 3H), δ 0.63 to δ 1.82 (m, 6H), δ 1.01 (d, 3H), and δ 4.62 (m, 1H). The material was used in subsequent reactions without further purification.

sec-Butylmethylmethoxysilane, 18.

To a solution of 2.00 ml (49.5 mmole) of methanol and 6.00 ml (50.9 mmole) of quinoline in 40 ml of pentane held in an ice bath was added with stirring a solution of 6.21 g (45.5 mmole) of sec-butylmethylchlorosilane in 20 ml of pentane. After addition was complete the ice bath was removed and stirring continued 2 h. The quinoline hydrochloride was removed by filtration. Distillation of the filtrate yielded 4.0 g (67% yield) of 18, bp 64-5°/144-5 mm; NMR (CCl_4, external TMS): δ 0.02 (d, 3H), δ 0.43 to δ 1.80 (m, 9H), δ 3.37 (s, 3H), and δ 4.35 (m, 1H); IR (film): 2900 s, 2080 s, 1440 m, 1360 w, 1230 m, 1180 w, 1080 s, 860 s, and 745 m; mass spectrum: 132(1), 131(9), 77(10), 75(100), 74(14), 61(14), and 45(13); Anal. calc'd for $C_6H_{18}OSi$: C, 54.48; H, 12.10. Found: C, 54.70; H, 12.30.

sec-Butylmethyldimethoxysilane, 19.

To a solution of 20.0 g (0.147 mole) of methyltrimethoxysilane in 50 ml of dry ether was added with stirring a solution of sec-butylmagnesium bromide obtained from 20.1 g (0.147 mole) of 2-bromobutane and 5.0 g (0.21 g-atom) of magnesium turnings in

300 ml dry ether. After refluxing and stirring 2 hours the mixture was filtered under nitrogen. The filtrate was distilled yielding a fraction, bp 54-8°/28 mm, which was redistilled to give 2.42 g (10% yield) of 19, bp 75-6°/65-66 mm (Lit.[100] bp 49-50°/24 mm); NMR (CCl_4, external TMS): δ -0.08 (s, 3H), δ 0.62 to δ 1.90 (m, 9H), and δ 3.41 (s, 6H); IR (film), 1460 s, 1375 m, 1250 s, 1210 m, 1180 s, 1090 s, 1000 m, and 970 w; mass spectrum: 162(1), 105(100), 75(27), 59(7), 45(5), and metastables at 53.6 and 68.0; Anal. calc'd for $C_7H_{18}O_2Si$: C, 51.80; H, 11.18; Si, 17.31. Found: C, 51.62; H, 11.14; Si, 17.42.

1,3-di(sec-butyl)-1,3-dimethyldisiloxane, 20.

To 25 ml of water containing 3.5 g of sodium bicarbonate was added 6.4 g (47 mmole) of sec-butylmethylchlorosilane in 50 ml of ether. After shaking 10 min the aqueous layer was removed, the ether layer washed once with diluted (ca. 0.02 M) hydrochloric acid, once with water, and dried over magnesium sulfate. Distillation gave a fraction, bp 85-8°/27-8 mm, which was redistilled to give 1.68 g (33% yield) of 20, bp 87-9°/30-31 mm; NMR (CCl_4, external TMS): δ 0.12 (d, 6H), δ 0.78 to 1.95 (m, 18H), and δ 4.50 (m, 2H); IR (film): 2110 s, 1460 m, 1375 w, 1250 s, 1210 w, 1065 s, 885 s, and 850 s; mass spectrum: 218(2), 161(49), 147(3), 133(6), 119(63), 105(100), 103(11), 91(6), and metastables at 88.0 and 68.5; Anal. calc'd for $C_{10}H_{26}OSi_2$: C, 54.97; H, 11.99; Si, 25.71. Found: C, 54.80; H, 11.96; Si, 25.96.

1,3-di(sec-butyl)-1,3-dimethyl-1-methoxydisiloxane, 21.

To 15 ml of a 1.8×10^{-2} M solution of potassium hydroxide in 95% aqueous methanol held in an ice bath was added 0.78 g of 1,2-dimethyl-1-silacyclobutane. When the evolution of hydrogen had ceased 20 ml of ether was added and all solvent removed under reduced pressure. The remaining oil was dissolved in ether and dried over magnesium sulfate. Removal of the solvent gave an oil which was purified by elution with hexane on a silica gel thick layer chromatographic plate. The component with R_f 0.50 was extracted with ether, the solvent removed and the remaining liquid distilled by molecular distillation, 115°/18-19 mm, to yield ca. 0.15 g of 21; NMR (CCl_4, internal benzene) (100 MHz): δ 0.00 (s, 3H), δ 0.14 (d, 3H), δ 0.47 to δ 1.66 (m, 18H), δ 3.42 (s, 3H), and δ 4.55 (m, 1H); IR (film): 2100 s, 1450 s, 1400 w, 1360 m, 1330 w, 1250 s, and 1060 s; mass spectrum: 248(<1), 233(2), 191(89), 135(100), 119(19), 105(22), 59(13), and metastables at 95.5 and 82.0; Anal. calc'd for $C_{11}H_{28}O_2Si_2$: C, 53.16; H, 11.36; Si, 22.60. Found: C, 53.36; H, 11.38; Si, 22.57.

Attempted Isomerization of cis-1,2-Dimethyl-1-silacyclobutane (10a).

To 1.0 ml of 95% aqueous methanol was added 0.10 ml of 99% isomerically pure 10a and 5 μl of toluene, as an internal standard. To this stirred solution held in an ice bath was added 1.0 ml of 3.2×10^{-4} M potassium hydroxide in 95% aqueous methanol. After 60 sec the reaction was stopped by acidifying with 0.25 ml of 3.2×10^{-3} M hydrochloric acid in 95% aqueous methanol. Glpc

analysis (16' x 1/8" column of 15% Apiezon L on 60-80 mesh chromosorb W; 90° to 125° at 10°/min, initial time of 3 min) showed that 75% of 10a had reacted (2 half-lives) and that ca. 35% of the original very small amount of 10b had also reacted, as determined by comparison with a glpc trace obtained before reaction. Solutions of a 60:40 mixture of 10a and 10b, respectively, in 95% aqueous methanol and in acidified 95% aqueous methanol showed no reaction of either isomer over a 14 hour period. Glpc analysis (on the column described above; 90° to 180° at 20°/min) showed nine products were formed in the reaction. Their retention times (min) are: 3.5, 4.8, 8.4, 9.3, 9.6, 11.1, 12.4, 13.0, and 15.4. By glpc mass spectral analysis and comparison of retention times the products with retention times of 3.5, 4.8, 8.4, and 11.1 min were identified as 18, 19, 20, and 21, respectively. The product with retention time 9.3 min has tentatively been identified as 23. Mass spectrum 216(<1), 201(1), 188(3), 161(10), 160(18), 159(100), 145(5), 133(9), 132(9), 131(20), 119(19), 117(36), 105(12), 103(15), and a metastable at 108.

Kinetic Measurements of Solvolysis of Silanes.

The apparatus used for most kinetics measurements was an 8 ml vial equipped with magnetic stirrer and septum and connected to a gas buret by use of thick wall tubing and 15 gauge needle. The vial was held in an ice bath at 0° and the hydrogen evolved was collected over water at 25°. In a typical determination 1.90 ml of a solution of potassium hydroxide in 95% aqueous methanol and 0.100 ml of silane were used, the neat silane being added via

syringe. At least 20 points were determined per run. The original concentration of silane was determined from the total quantity of hydrogen evolved after about 10 half-lives. For solvolysis of 18, the procedure was identical except that a 125 ml flask was substituted for the vial.

The pseudo-first-order rate constant, k′, was obtained from a plot of Equation 3-2,[74] where 't' is time in sec, 'V_∞' is the total

EQUATION 3-2

$$\ln \frac{V_\infty}{V_\infty - V} = k't$$

volume of H_2 evolved, and 'V' is the volume evolved at time 't'. The second-order-rate constants k were obtained from Equation 3-3.

EQUATION 3-3

$$k = \frac{k'}{[OH^-]}$$

Kinetics of Isomerization of 10a.

The apparatus used for kinetic measurements of isomerization of 10a was a 3 ml vial equipped with a septum and held in a water bath at 23°. Solutions of potassium cyanide were prepared by dilutions of a DMF solution saturated with KCN. The DMF had been distilled in the dark and all solutions were stored in the dark. Since absolute concentrations were unknown only relative concentrations are reported. All runs were made by adding via syringe

0.025 ml of 10a to 0.50 ml of a solution of KCN in DMF. The reaction was followed by periodically withdrawing a sample and analyzing immediately by glpc on the 16' x 1/8" Apiezon L column previously described. The equilibrium constant K_{eq} was determined by allowing the reaction to proceed for at least 10 half-lives. For isomerization of 10a to 10b, K_{eq} equals 1.15.

The pseudo-first-order rate constants, k_1, were obtained from a plot of Equation 3-4,[101] where 'A_0' is the initial

EQUATION 3-4

$$\ln \left[\frac{A_0-Ae}{A-Ae}\right] = (k_1 + k_{-1})t$$

concentration of silane, 'Ae' the concentration of 10a at equilibrium, 'A' the concentration of 10a at time 't', and k_1 and k_{-1} are the rate constants for the forward and reverse reactions, respectively. Since the percent of each isomer was proportional to its concentration, percent was substituted for concentration. Actually, an observed rate constant k' was obtained, which is the sum of k_1 and k_{-1}, from which k_1 could be calculated using Equation 3-5.

EQUATION 3-5

$$k_{-1} = \frac{k_1}{K_{eq}}$$

CHAPTER IV

SOLVENT-INDUCED ISOMERIZATION OF HALOSILACYCLOBUTANES

Siliconium ions with an sp^2 structure, analogous to carbonium ions, have never been isolated or observed as reaction intermediates.[6,*] What at first appeared to be convincing evidence for their existence was the racemization of chlorosilanes in solvents of high dielectric constants such as acetonitrile and nitromethane.[1] Sommer proposed the formation of a siliconium ion in an ion pair to explain the racemization, the necessity of restricting it to an ion pair being dictated by the weak conductivity of the reaction media.

Corriu and co-workers have extensively studied the racemization of a number of chlorosilanes with various solvents.[6,35,103-105] There are numerous solvents that effect racemization, including: ethers such as dioxane, tetrahydrofuran, and diethyl ether; esters such as ethyl acetate and ethyl benzoate; and polar aprotic solvents such as HMPT, DMF and DMSO.

That the racemization does not involve an sp^2 siliconium ion was demonstrated by Corriu in a study of the effect of steric hindrance on the rates of racemization with HMPT of a series of alkyl substituted silanes, αNpPhClSiR. The following order of relative rate constants was observed: R = Me > Et > Pr > i-Pr > t-Bu.[6] The reverse order of reactivity would be predicted for ionization

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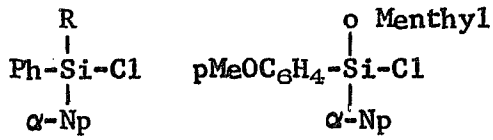
*Recently, the reaction of 5-(p-dimethylaminophenyl)-5H-dibenzo[b,f]silepin with triphenylmethyl perchlorate was suggested to lead to a siliconium ion.[102]

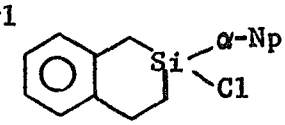
to an sp^2 siliconium ion since steric hindrance would be relieved. The results are in agreement with a mechanism involving coordination of the solvent to the silicon. Such coordination of the basic part of solvent molecules with the available 3 d-orbitals on silicon has been suggested as the reason for large solvent effects on the o.r.d. curves of several asymmetric tetraorganosilanes,[106] and a large number of complexes of polar aprotic solvents with halosilanes are known.[107,108]

In a study using seven different asymmetric silanes, 24 through 30, the racemization with DMF, DMSO, and HMPT was shown to be second-order in solvent and first-order in chlorosilane.[104]



24 to 28

29



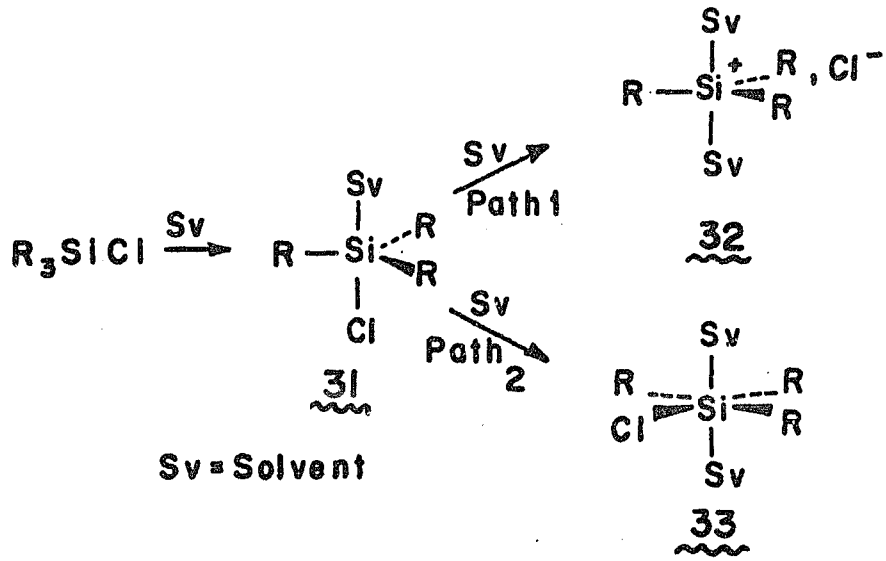
30

R = Me 24
R = Et 25
R = i-Pr 26
R = neo-pentyl 27
R = Menthoxy 28

Bromosilanes gave similar results.[109]

On these bases Corriu proposed two possible mechanisms, both involving an initial coordination of one solvent (Sv) molecule to silicon to form a pentacoordinate complex, 31, (Scheme 4-1)

SCHEME 4-1



followed by addition of a second solvent molecule either to displace chloride ion to give 32 (path 1) or form a hexacoordinate species, 33 (path 2). Either pathway would result in isomerization since both 32 and 33 are symmetrical.

In an effort to determine which mechanism was operating, substituent effects were determined by Corriu for a series of arylchlorosilanes.[105] A small increase (<2) in the rate was observed for the strong electron-donating p-methoxy group relative to hydrogen, but no racemization was observed with the strong electron-withdrawing trifluoromethyl substituent. Corriu argued that the small effect of the p-methoxy substituent favored path 2 (Scheme 4-1), but failed to explain the effect of the trifluoromethyl substituent. The latter, along with the decreased rates observed in the series ≡Si-Br > Si-Cl > Si-F are in accord with path 1.[105]

To decide which mechanism was operating, a study of the isomerization of cis-1,2-dimethyl-1-chloro-1-silacyclobutane, 7a, was undertaken. If path 1 (Scheme 4-1) were operating, then 7 should react much slower than acyclic or larger ring chlorosilanes since the C-Si-C angle in 32 is ca. 120°, but in 7 is restricted to ca. 90°. Conversely, if path 2 (Scheme 4-1) were operating then 7 should show increased reactivity over other chlorosilanes since the C-Si-C angle in 33 is already ca. 90°. For the same reason that 7 may not form 32, 7 may not form 31; thus, 7 may react by a different mechanism from other chlorosilanes. Such a mechanism may involve interconversion of isomeric trigonal bipyramids by Berry pseudorotation or turnstile rotation and allow 7 to react by an ionization mechanism analogous to path 1. The presence of the naphthyl and other bulky groups undoubtedly has a large steric effect on the reactivity of 24 through 30; thus, a direct comparison to 7 would not be possible. For this reason the kinetics of isomerization of 1,2-dimethyl-1-chlorosilacyclopentane is currently being investigated in order that a determination of the effect of angle strain may be made.[110]

Most of the solvents that have previously been shown to racemize chlorosilanes isomerized 7a, acetonitrile being an exception. Sulfolane, pyridine, and quinoline, all of which also isomerized 7a, have not been reported previously. That quinoline isomerized 7a was interesting in the respect that it was used as the HCl acceptor in the reaction of alcohols with 7 when evidence for a "stereomutation" mechanism was presented.[26] Thus the reaction of

$\frac{n}{2}$ moles of alcohol with n moles of a 50:50 mixture of 7a and 7b to give an unequal ratio of isomeric alkoxy products and the recovered 7a and 7b still present in an equal ratio would be observed if 7a and 7b reacted at different rates but were isomerized by quinoline.

The solvent system HMPT in carbon tetrachloride was chosen for careful study since the majority of the work previously reported was with this system, and DMF and DMSO apparently reacted with 7. The nature of the products has not been determined but they are probably siloxanes as has previously been observed in the reaction of DMSO and DMF with chlorosilanes.[111,112] The rate of the pseudo-first-order isomerization was followed by NMR spectroscopy as described in the experimental section.

The effect of changing HMPT concentration is shown in Table 4-1. A plot of log k_1 against log[HMPT] concentration (Figure

TABLE 4-1

Pseudo-first-order Rate Constants at Various HMPT Concentrations.[a]

10^5 x [HMPT] M	10^4 x k_1 [b,c] sec^{-1}
200.	36.
100.	16.
50.	8.0
25.	3.1
10.	1.1
5.0	0.43
2.5	0.15

[a] 0.75 M in 7. [b] Specific rate data are given in Appendix B.
[c] $45^\circ \pm 1^\circ$.

4-1) gave a good straight line from which an apparent order of 1.23 ± 0.05 in HMPT was calculated. That no other molecule of chlorosilane was involved in the rate-determining step was demonstrated by determining k_1 at different chlorosilane concentrations. Since the method used in following the reaction limited the range of possible chlorosilane concentrations, k_1 was determined for only three concentrations of chlorosilane but was checked at various HMPT concentrations. The results (Table 4-2) showed that

TABLE 4-2

Pseudo-first-order Rate Constants at Various Chlorsilane Concentrations.

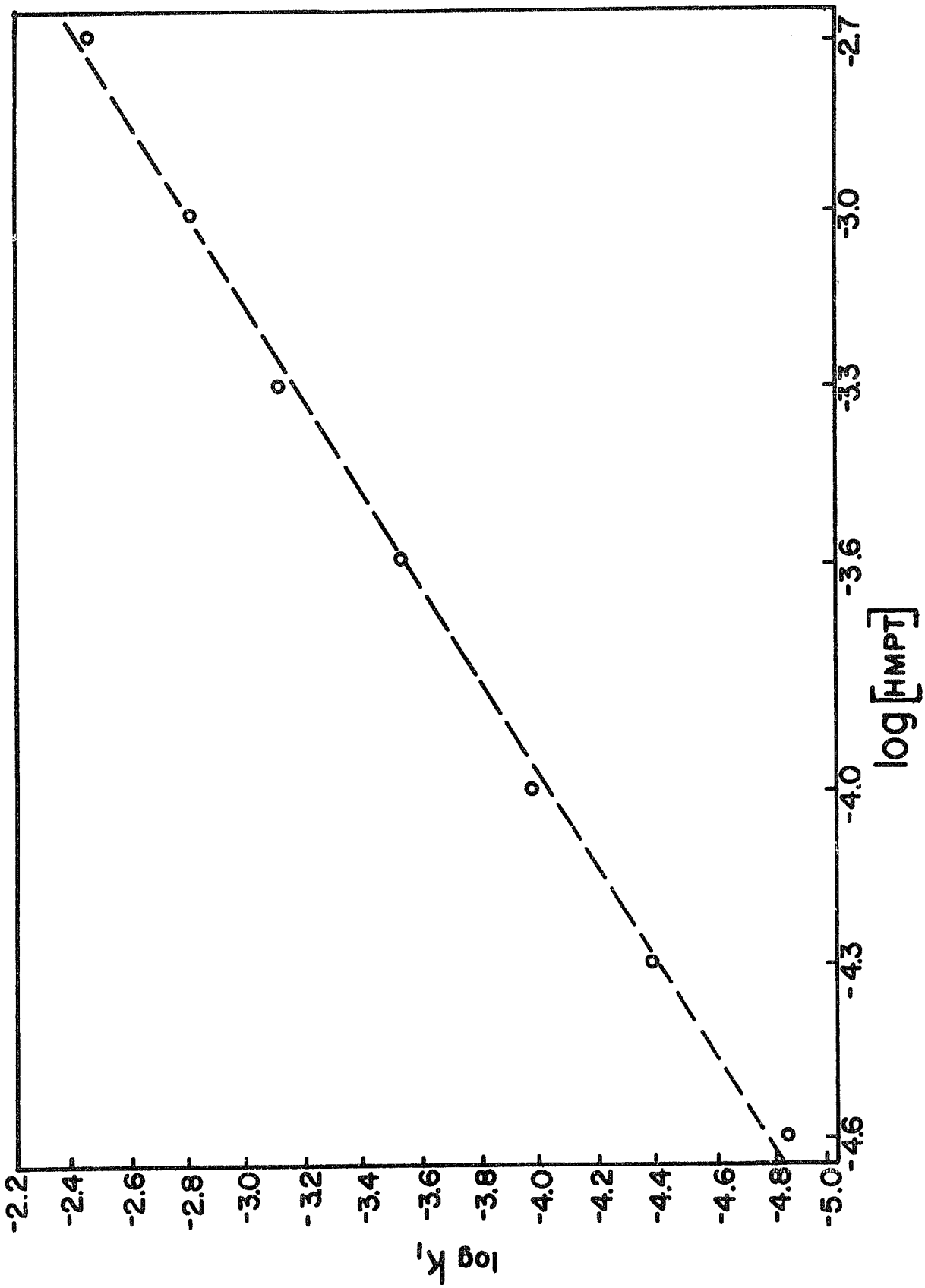
$10^4 \times$ [HMPT] M	[$\widetilde{M}$]	$10^4 \times k_1$ [a,b] sec^{-1}
10.	0.75	16.
10.	0.30	14.
5.0	1.13	9.7
5.0	0.75	8.0
5.0	0.30	6.6
2.5	0.75	3.1
2.5	0.30	2.6
1.0	0.75	1.1
1.0	0.30	1.1

[a] Specific rate data are given in Appendix B.

[b] $45^\circ \pm 1^\circ$.

although generally the rate increased slightly with increasing

FIGURE 4-1. Plot of log k_1 vs. log[HMPT] for isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane. Data taken from Table 4-1.


log k1
-2.2
-2.4
-2.6
-2.8
-3.0
-3.2
-3.4
-3.6
-3.8
-4.0
-4.2
-4.4
-4.6
-4.8
-5.0
log [HMPT]
-2.7
-3.0
-3.3
-3.6
-4.0
-4.3
-4.6

chlorosilane concentration, the difference was insufficient to warrant the inclusion of chlorosilane concentration in the pseudo-first-order rate constant. It seemed most reasonable to attribute the small rate increase to a change in solvent polarity due to the increasing chlorosilane concentration.

Activation parameters (Table 4-3) for the isomerization were

TABLE 4-3

Activation Parameters

E_a (kcal/mole)	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$ (e.u.)
11.1 ± 1.0	10.5 ± 1.0	-40.5 ± 1.6

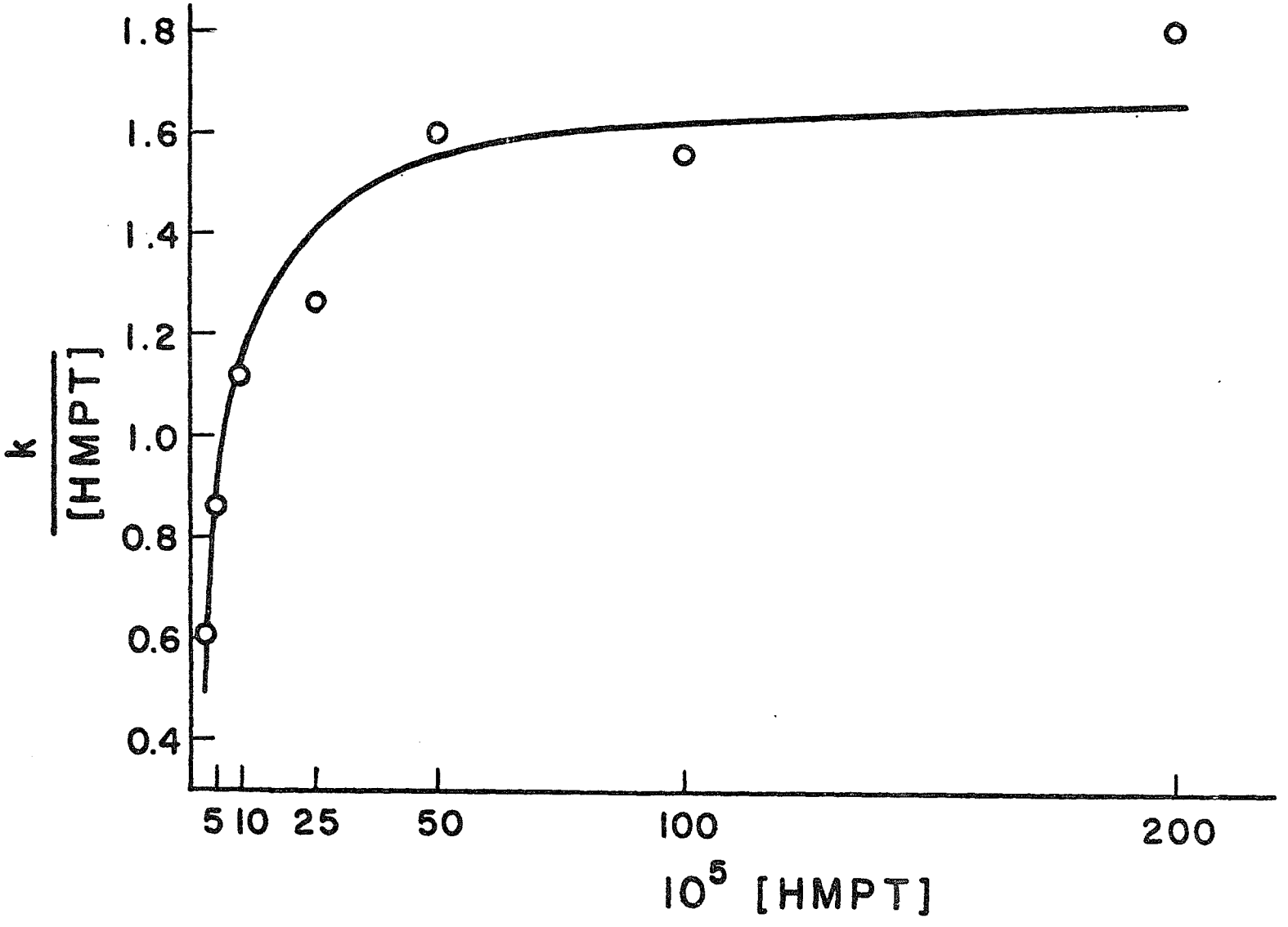
determined from the variation in k_1 over the range 271 to 329°K at a HMPT concentration of 5×10^{-4} M. Although $\Delta H^{\ddagger}$ for the isomerization of I was substantially greater than the values of 0-3 kcal/mole reported for acyclic chlorosilanes[104] this difference may only reflect the greater barrier to inversion in small ring systems rather than a change in mechanism.

The observed order of 1.23 in HMPT was surprising and at first suggested that the observed rate, k_1, was the sum of a first-order reaction and a second-order reaction in HMPT (Equation 4-1). However, a plot of $k_1/[HMPT]$ vs. [HMPT] (Figure 4-2) was

EQUATION 4-1

$$k_1 = k_a[HMPT] + k_b[HMPT]^2$$

FIGURE 4-2. Plot of $k_1/[HMPT]$ vs. [HMPT] for isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane. Data taken from Table 4-1.


1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
k / [HMPT]
5 10 25 50 100 200
10^5 [HMPT]

non-linear which was inconsistent with this scheme. Inspection of Figure 4-2 revealed that above ca. 5×10^{-4} M in HMPT the reaction became first-order in HMPT (slope ~0) but at lower concentrations the reaction was becoming second-order in HMPT. Close inspection of Figure 4-1 led to the same conclusion. This behavior was consistent with a two-step formation of an intermediate, presumably either 32 or 33 (Reaction 4-1). Application of the steady state

REACTION 4-1

$$R_3SiCl + Sv \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} R_3Si\begin{matrix}Cl\\ \diagup\\ \diagdown\\ Sv\end{matrix} \xrightarrow[Sv]{k_5} 32 \text{ or } 33$$

34

assumption to the intermediate 34 yields the kinetic law of Equation 4-2, and the observed rate constant, k_1, is therefore defined as

EQUATION 4-2

$$\text{rate} = \frac{k_4 k_5 [Sv]^2 [R_3SiCl]}{k_{-4} + k_5[Sv]}$$

Equation 4-3. The line shown in Figure 4-2 is a plot of Equation 4-3

EQUATION 4-3

$$k_1 = \frac{k_4 k_5 [Sv]^2}{k_{-4} + k_5[Sv]}$$

with $k_4 = 1.7\ M^{-1}\ sec^{-1}$ and $k_5/k_{-4} = 2 \times 10^4\ M^{-1}$.

The same kinetic scheme has been used to explain the apparent change in the rate-determining step in hydrolysis of aryloxytriphenylsilanes.[113] However, the kinetic data from that study have recently been challenged.[114]

At low concentrations of HMPT ($<10^{-5}$ M), the term $k_5[Sv]$ in Equation 4-3 becomes small relative to k_{-4} and, therefore, negligible. The observed rate constant k_1 is then defined as Equation 4-4 and a third-order rate constant k_3 can be introduced

EQUATION 4-4

$$k_1 = \frac{k_4 k_5 [Sv]^2}{k_{-4}}$$

(Equation 4-5). This is in good agreement with

EQUATION 4-5

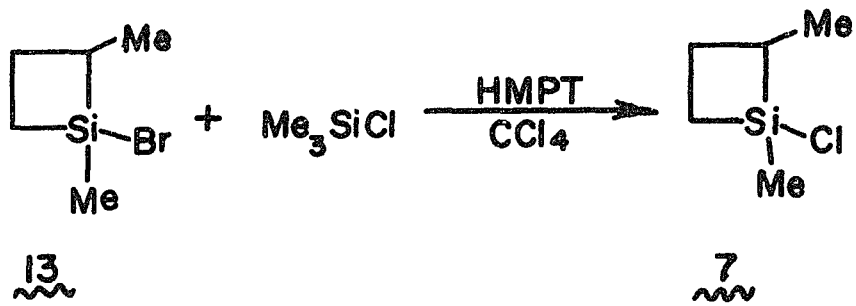
$$k_3 = \frac{k_1}{[Sv]^2} = \frac{k_4 k_5}{k_{-4}} = 3.4 \times 10^4\ M^{-2}\ sec^{-1}$$

$k_1/[Sv]^2 = 2.4 \times 10^4\ M^{-2}\ sec^{-1}$ for the reaction at 2.5×10^{-5} M in HMPT, where it is approaching second-order in HMPT. Comparison of k_3 with the third-order rate constant reported by Corriu for the racemization of i-PrPhNpSiCl (26) with HMPT ($k_3 \approx 4 \times 10^{-2}\ M^{-2}\ sec^{-1}$) revealed that 7a reacted ca. 5×10^5 times faster.[104] Such a difference in reactivity seems too large to attribute solely to steric effects, and thus, this difference, in part, apparently is due to the geometry of the silacyclobutane ring. Final resolution of

this question, however, awaits the results of the study of the silacyclopentane system.

The greater reactivity of 7a over 26 suggested that the formation of the hexacoordinate intermediate 33 rather than the ionic intermediate 32 is the mechanism of isomerization, yet evidence for the latter was found in the halide-halide exchange observed between 1-bromo-1,2-dimethyl-1-silacyclobutane (13) and trimethylchlorosilane (Reaction 4-2), catalyzed by HMPT. No exchange occurred in the

REACTION 4-2



13 7

absence of HMPT. A similar fluoride-chloride exchange using Ph_3P as catalyst has previously been observed[115] (Reaction 4-3).

REACTION 4-3

$$2\ Me_3SiCl + MePhSiF_2 \xrightarrow{Ph_3P} 2\ Me_3SiF + MePhSiCl_2$$

The rapid halide-halide exchange observed in Reaction 4-2 suggested an alternate mechanism involving an initial displacement of chloride ion by one or more solvent molecules (Reaction 4-4a),

followed by a rate-determining step in which chloride-chloride exchange with inversion (Reaction 4-4b). Walden inversions

REACTION 4-4

$$R_3SiCl + n\ Sv \rightarrow [R_3Si(Sv)n]^+,\ Cl^- \qquad (a)$$

$$R_3SiCl + Cl^- \rightarrow R_3SiCl + Cl^- \qquad (b)$$

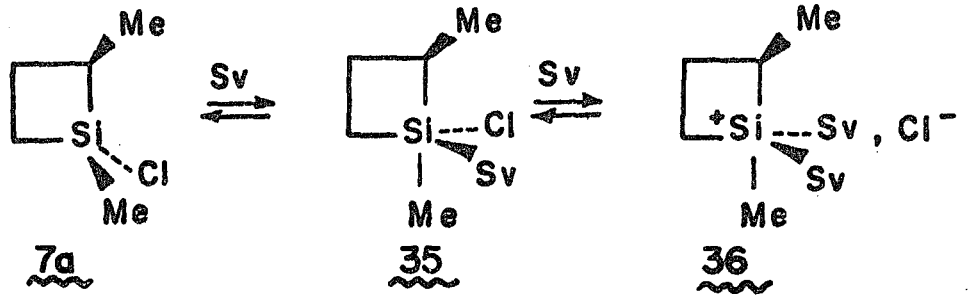
such as the latter step are well known for halosilanes,[1,6] and precedents for the first step exist in the numerous solvent adducts known for halosilanes with DMF, DMSO, acetonitrile, trimethylphosphine oxide, and amines.[108] The organic base adducts of the bromo- and iodosilanes are known to be ionic from conductivity and infrared measurements.[116,117] Data for chlorosilane adducts indicates ionic structures also.[108]

The mechanism depicted in Reaction 4-4 fully explained the rapid halide-halide exchange observed in Reaction 4-2 and was compatible with steric effects, substituent effects, and the order of reactivity of the various halides observed in solvent induced racemization. Furthermore, the activation parameters reported for halide-halide exchange,[118,119] ($\Delta H^{\ddagger}$ = 2 to 12 kcal/mole and $\Delta S^{\ddagger}$ = -40 to -60 e.u.) correspond closely to the activation parameters reported for solvent racemization of chlorosilanes. The observation that tetrabutylammonium bromide isomerized $\underset{\sim}{7}$ at a rate only slightly greater than that caused by an equivalent concentration of HMPT was apparently convincing evidence for this mechanism. However, the kinetics observed herein defy explanation in terms of such a mechanism.

The possibility exists that the halide-halide exchange observed in Reaction 4-2 occurred through some mechanism unrelated to isomerization. But in view of the comparable rates of exchange and isomerization both apparently occur through a common intermediate. The following mechanism appears to be in accord with all data: reversible coordination of two solvent molecules with displacement of chloride ion, as in path 1 (Scheme 4-1), accounting for isomerization; halide-halide exchange occurring as in Reaction 4-4b but with predominant retention of configuration. That halide-halide exchange would occur with predominant retention is consistent with the known stereochemistry of reactions at silicon in small rings (Chapter II). Furthermore, chloride-chloride exchange in benzene (a solvent similar in polarity to CCl_4) has been shown to proceed with almost complete retention of configuration.[119]

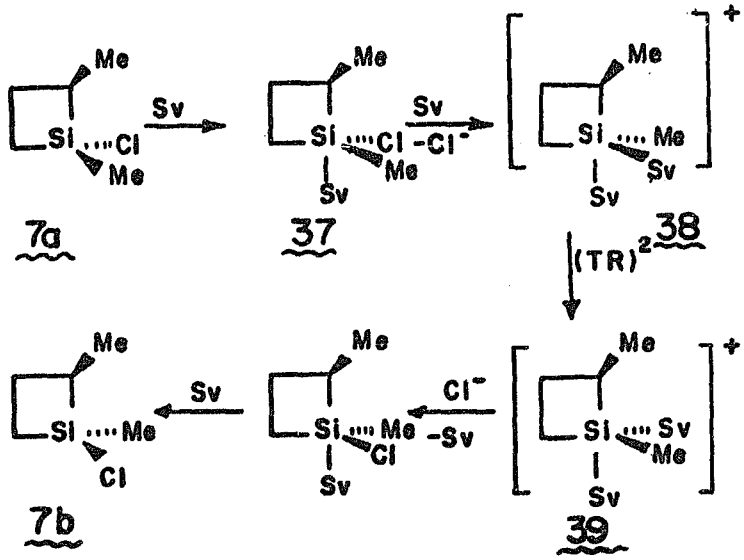
31 and 32, are inconsistent with the reactivity of 7, since both 31 and 32 require C-Si-C angles of ca. 120°. Although 31 and 32 may well be the structures for intermediates in the reactions of large ring and acyclic chlorosilanes, the small angle in four and five-member rings requires apical-equatorial placement of the ring.[64,66] A plausible pathway for the isomerization of 7a is shown in Scheme 4-2. The formation of 35 is inconsistent, however,

SCHEME 4-2



with the postulate in phosphorus chemistry of apical entry and departure of nucleophiles.[64,65] A more reasonable possibility is axial entry of Sv to give 37 (Scheme 4-3) followed by displacement

SCHEME 4-3



of chloride ion by back-side attack to give 38. A double turnstile rotation[64,65] followed by essentially the reverse of the first two

steps would result in formation of the trans isomer 7b. Halide-halide exchange could occur between an ionic intermediate, 38 or 39, which presumably are ion pairs, and another halosilane molecule (Reaction 4-4b).

CHAPTER IV

EXPERIMENTAL

Isomerization of 7a with Various Solvents.

In general the isomerization of 7 with various solvents was determined by adding ca. 0.1 ml of the solvent to 1 ml of an 85:15 mixture of 7a and 7b in CCl_4 and observing any change in the ratio by NMR at ambient temperature. Pyridine, quinoline, DMSO, DMF, and HMPT gave complete isomerization in < 1h. Sulfolane and nitromethane required ca. 24h while acetonitrile gave no isomerization after 18h. THF and acetone gave no isomerization of 7 at room temperature but when a sample of 7 containing a trace of either THF or acetone was held at 115° for 2h isomerization was complete.

Kinetic Measurements.

In all cases the reaction was followed by NMR. The standard procedure was to place in a dry NMR tube via syringe 0.50 ml of a solution of known concentration of 7 in CCl_4 (7a to 7b ratio of 85:15). The tube was placed in the cavity of an A60A NMR Spectrometer held at 45°±1°. After allowing ca. 5 minutes for the temperature to equilibrate, 0.50 ml of a solution of known concentration of hexamethylphosphoric triamide (HMPT) in CCl_4 was added via syringe. At definite time intervals the Si-Me region (δ 0.35 to δ 0.60) was integrated on a 100 Hz sweep width to obtain the ratio of 7a to 7b. The reaction was followed until ca. a 54:46 ratio of 7a to 7b was obtained or until at least 35 points were

taken. The equilibrium constant (K_{eq}) for the isomerization of 7a to 7b was determined by allowing three different runs to proceed for at least 10 half-lives and then repeatedly integrating the sample. From an average of the 18 integrations made, the equilibrium constant was determined to be 1.08.

From the data obtained as described above, the pseudo-first-order rate constants could be obtained by the method described for the kinetics of isomerization of 10a (Chapter III).

Activation Parameters.

Pseudo-first-order rate constants were determined as above at various temperatures. Activation parameters were determined in the usual manner by plotting log k_1 vs. $1/T$.[101]

Treatment of Data.

All points in which the sum of the integrations of 7a and 7b deviated greater than 1.96 times the standard deviation (σ) (95% confidence level) were discarded. Similarly, all points if any that deviated greater than 1.96 times the standard error of estimate ($S_{y.x}$), as determined by a regression analysis, were discarded. A second regression analysis thus provided the slope, 1.92 k_1. The reported error is 1.96 times the standard deviation of the slope (95% confidence level).

Halide-Halide Exchange Catalyzed by HMPT.

In a 25 ml flask equipped with a magnetic stirrer and set for distillation was placed 1.95 g (10.9 mmole) of 13, 2.4 g (21.8 mmole) of trimethylchlorosilane, and 10 ml of 2×10^{-4} M HMPT in CCl_4. After stirring 2 h at room temperature, the mixture contained ca. a 60:40 mixture of 13 and 7 respectively, as determined by NMR. Distillation gave a fraction, bp 60-8°/95 mn., the mass spectrum and NMR of which were identical to those of 7.

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APPENDIX A

Specific Rate Data for Solvolysis of Silanes and for Cyanide Induced Isomerization of 1,2-Dimethyl-1-silacyclobutane (described in Chapter III)

TABLE A-1

Solvolysis of cis-1,2-Dimethyl-1-silacyclobutane[a] (10a) in 95 Volume % Aqueous Methanol[b] at 0°.

Run 1

Time, sec	ml of H_2 evolved
8	1.6
15	2.1
22	3.1
28	3.6
35	4.1
43	4.6
54	5.1
66	5.6
82	6.1
98	6.5
112	6.8
125	7.0
138	7.2
154	7.4
172	7.6
650	8.3

[a] 0.078 g of 10a. [b] 1.50×10^{-4} M in KOH.

TABLE A-1a

Rate Constants Derived from Table A-1.

Run	$k' \times 10^2$, sec^{-1}	k, M^{-1} sec^{-1}	r
1	1.35 ± 0.04	$90. \pm 3.$	0.998

FIGURE A-1. Solvolysis of cis-1,2-Dimethyl-1-silacyclobutane. Data taken from Table A-1, run 1.

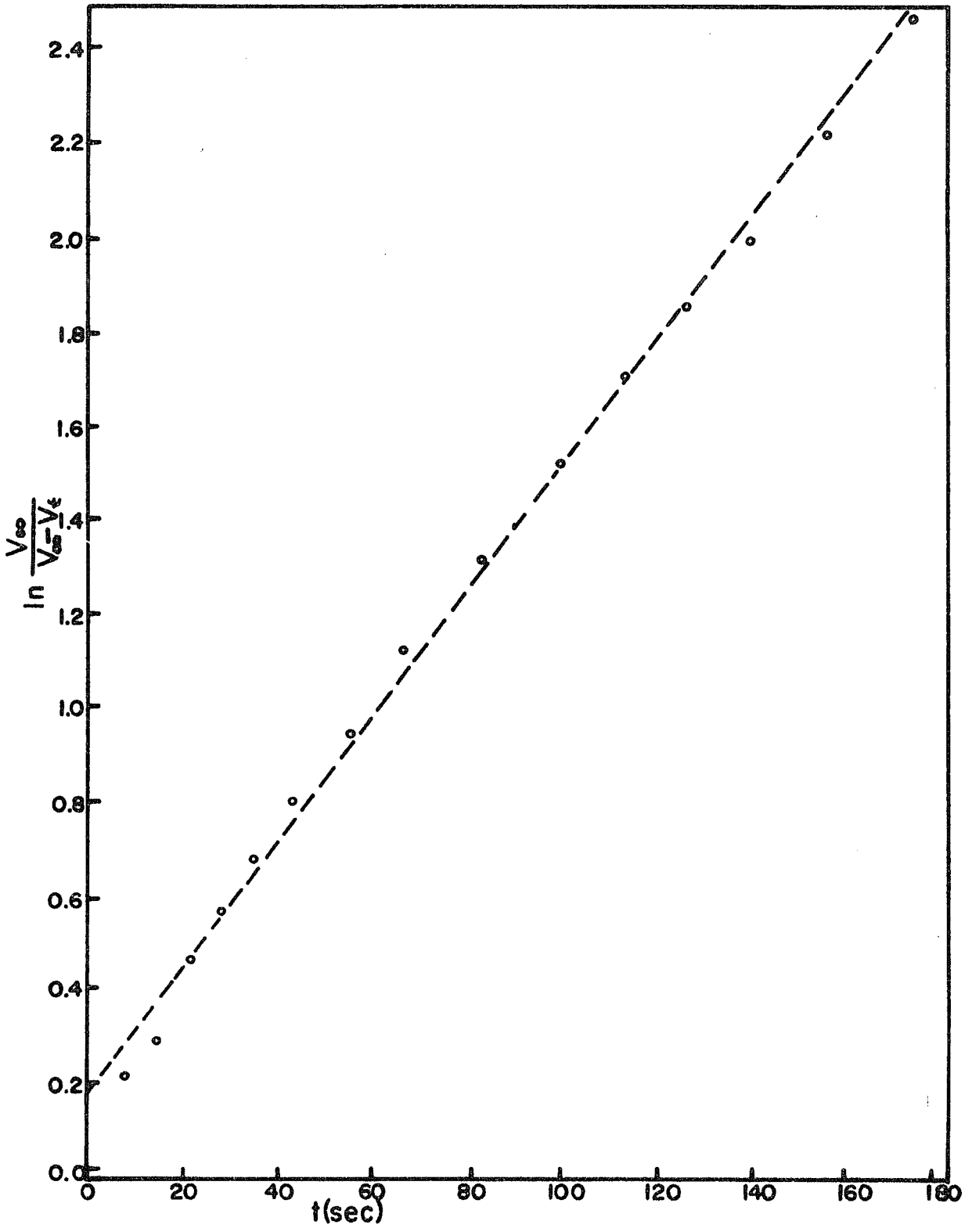


TABLE A-2

Solvolysis of trans-1,2-Dimethyl-1-silacyclobutane[a] (10b) in 95 Volume % Aqueous Methanol[b] at 0°.

Run 1	
Time, sec	ml of H_2 evolved
8	0.2
20	0.5
30	0.8
37	1.0
44	1.2
52	1.4
61	1.6
73	1.8
85	2.0
104	2.3
120	2.5
141	2.7
164	2.9
196	3.1
220	3.3
260	3.5
300	3.7
1150	4.5

[a] 0.078 g of 10b. [b] 1.50×10^{-4} M in KOH.

TABLE A-2a

Rate Constants Derived from Table A-2.

Run	$k' \times 10^3$, sec^{-1}	k, M^{-1} sec^{-1}	r
1	5.71 ± 0.22	$38. \pm 2.$	0.997

FIGURE A-2. Solvolysis of trans-1,2-Dimethyl-1-silacyclobutane. Data taken from Table A-2, run 1.

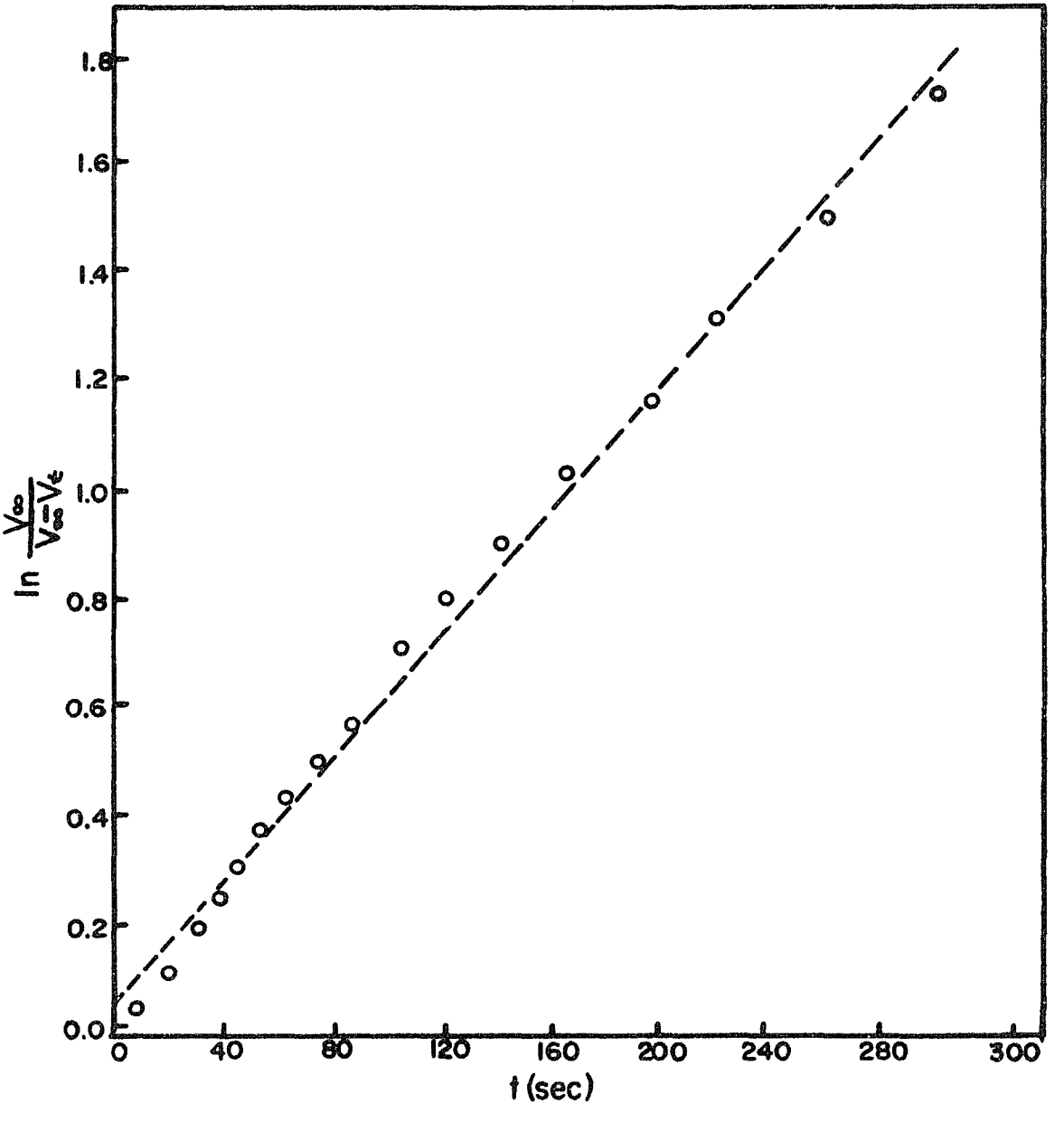


TABLE A-3

Solvolysis of sec-Butylmethylmethoxysilane[a] (18) in 95 Volume % Aqueous Methanol[b] at 0°.

Run 1		Run 1 (continued)	
Time, sec	ml of H_2 evolved	Time, sec	ml of H_2 evolved
11	2.5	125	31.0
16	3.5	136	33.0
22	5.0	147	35.0
29	7.0	158	37.0
36	9.0	171	39.0
42	11.0	191	42.0
50	13.0	204	44.0
57	15.0	220	46.0
64	17.0	237	48.0
72	19.0	255	50.0
80	21.0	273	52.0
88	23.0	294	54.0
96	25.0	318	56.0
106	27.0	347	58.0
115	29.0	1100	68.5

[a] 0.340 g of 18. [b] 0.201 M in KOH.

TABLE A-3a

Rate Constants Derived from Table A-3.

Run	$k' \times 10^3$, sec^{-1}	$k \times 10^2$, M^{-1} sec^{-1}	r
1	5.36 ± 0.07	2.66 ± 0.04	0.999

FIGURE A-3. Solvolysis of sec-Butylmethylmethoxysilane. Data taken from Table A-3, run 1.

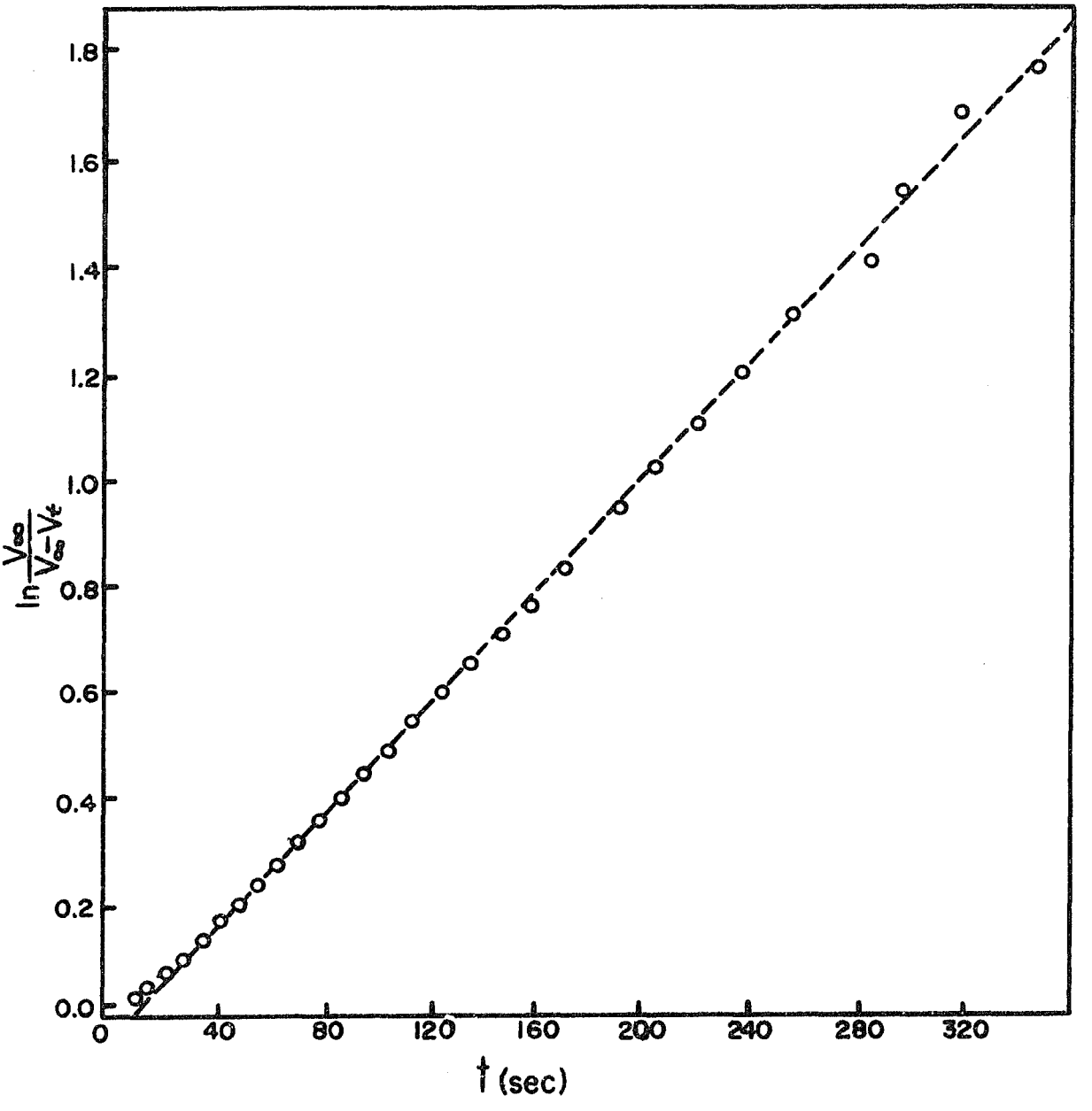


TABLE A-4

Solvolysis of 1,3-Di(sec-butyl)-1,3-dimethyldisiloxane[a] (20) in 95 Volume % Aqueous Methanol[b] at 0°.

Run 1		Run 1 (continued)	
Time, sec	ml of H_2 evolved	Time, sec	ml of H_2 evolved
10	0.7	182	9.3
25	1.3	194	9.8
41	2.3	207	10.3
50	2.8	219	10.8
60	3.3	233	11.3
69	3.8	248	11.8
81	4.5	262	12.3
93	5.1	277	12.8
106	5.8	294	13.3
116	6.3	310	13.8
127	6.8	327	14.3
138	7.8	348	14.8
159	8.3	1000	18.7
170	8.8		

[a]0.0813 g of 20. [b]0.815 M in KOH.

TABLE A-4a

Rate Constants Derived from Table A-4.

Run	$k' \times 10^3$, sec^{-1}	$k \times 10^3$, M^{-1} sec^{-1}	r
1	4.48 ± 0.15	5.50 ± 0.18	0.996

FIGURE A-4. Solvolysis of 1,3-Di(sec-butyl)-1,3-dimethyldisiloxane. Data taken from Table A-4, run 1.

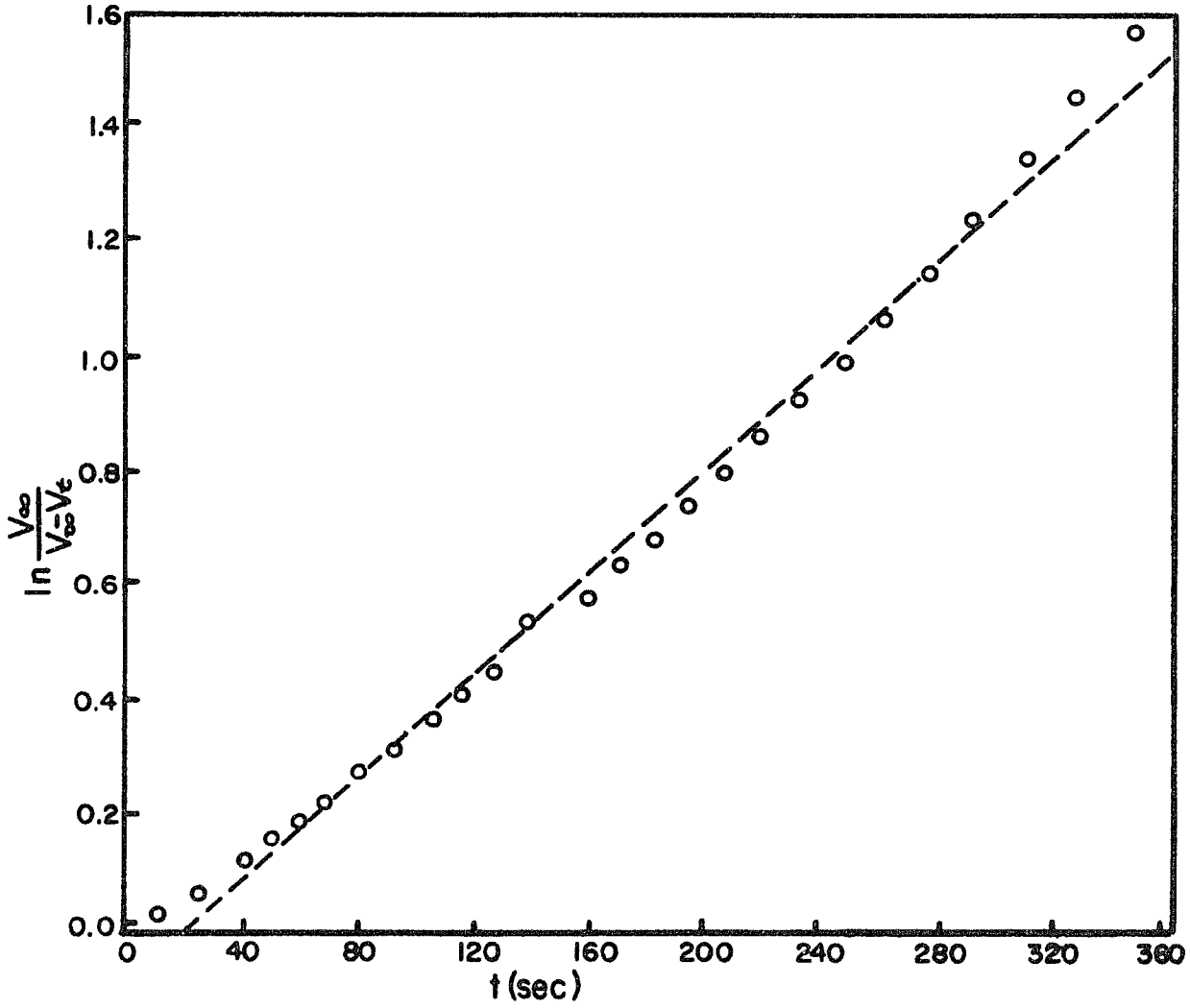


TABLE A-5

Isomerization of cis-1,2-Dimethyl-1-silacyclobutane (10a) with Potassium Cyanide[a] in DMF at 23°.

Run 1

Time, min	% 10a Remaining
24	61.9
38	57.6
57	52.6
76	46.1
153	46.9
169	46.1

[a]Relative concentration of 10.

TABLE A-5a

Rate Constants Derived from Table A-5

Run	$k' \times 10^2$, min^{-1}	$k_1 \times 10^2$, min^{-1}	r
1	2.74 ± 0.20	1.47 ± 0.11	0.993

FIGURE A-5. Isomerization of cis-1,2-Dimethyl-1-silacyclobutane with Potassium Cyanide. Data taken from Table A-5, run 1.

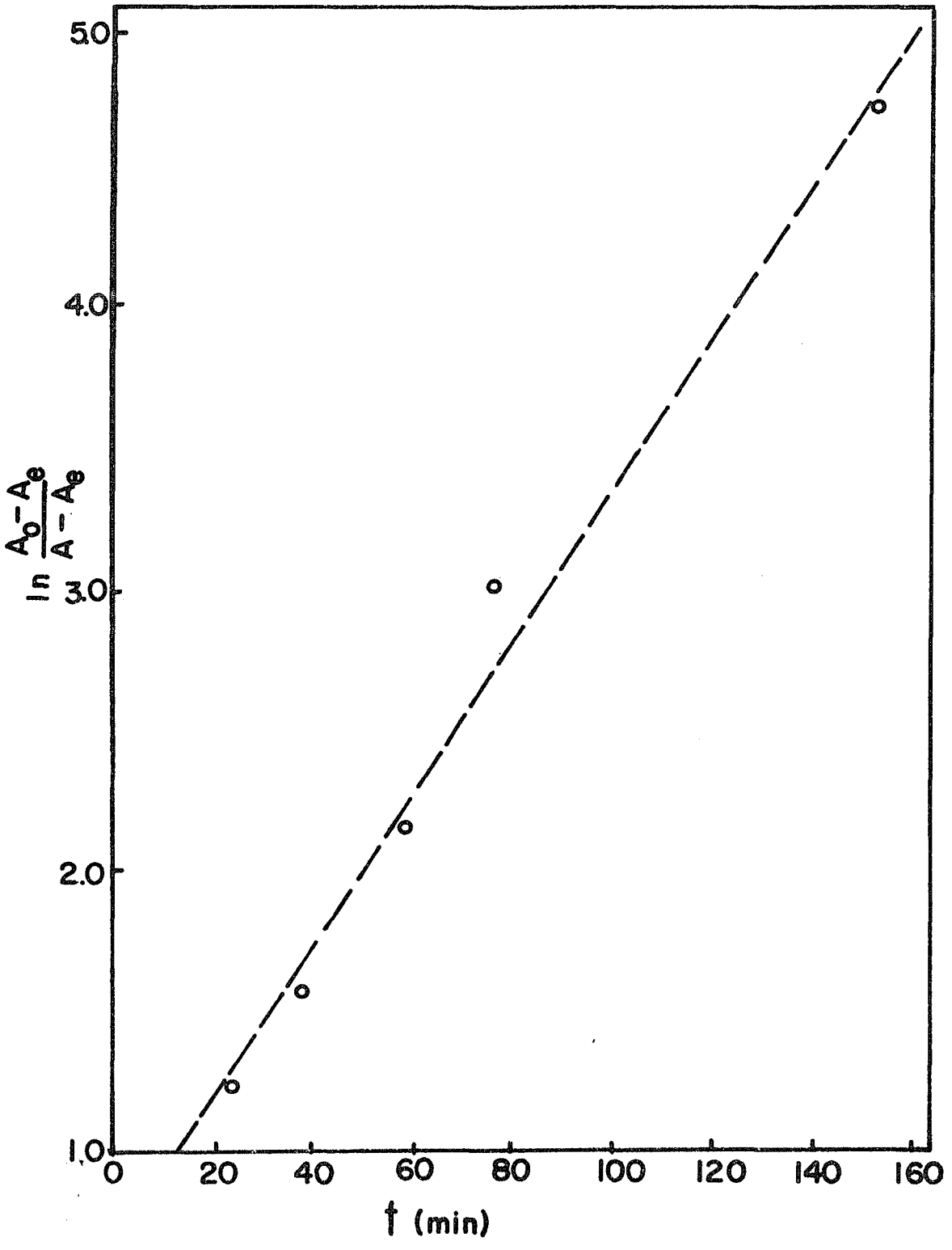


TABLE A-6

Isomerization of cis-1,2-Dimethyl-1-silacyclobutane (10a) with Potassium Cyanide[a] in DMF at 23°.

Run 1

Time, min	% 10a Remaining
8	87.7
29	78.5
46	72.9
64	66.7
84	63.4
125	56.2

[a]Relative concentration of 5.

TABLE A-6a

Rate Constants Derived from Table A-6.

Run	$k' \times 10^2$, min^{-1}	$k_1 \times 10^3$, min^{-1}	r
1	1.23 ± 0.05	6.58 ± 0.24	0.999

FIGURE A-6. Isomerization of cis-1,2-Dimethyl-1-silacyclobutane with Potassium Cyanide. Data taken from Table A-6, run 1.

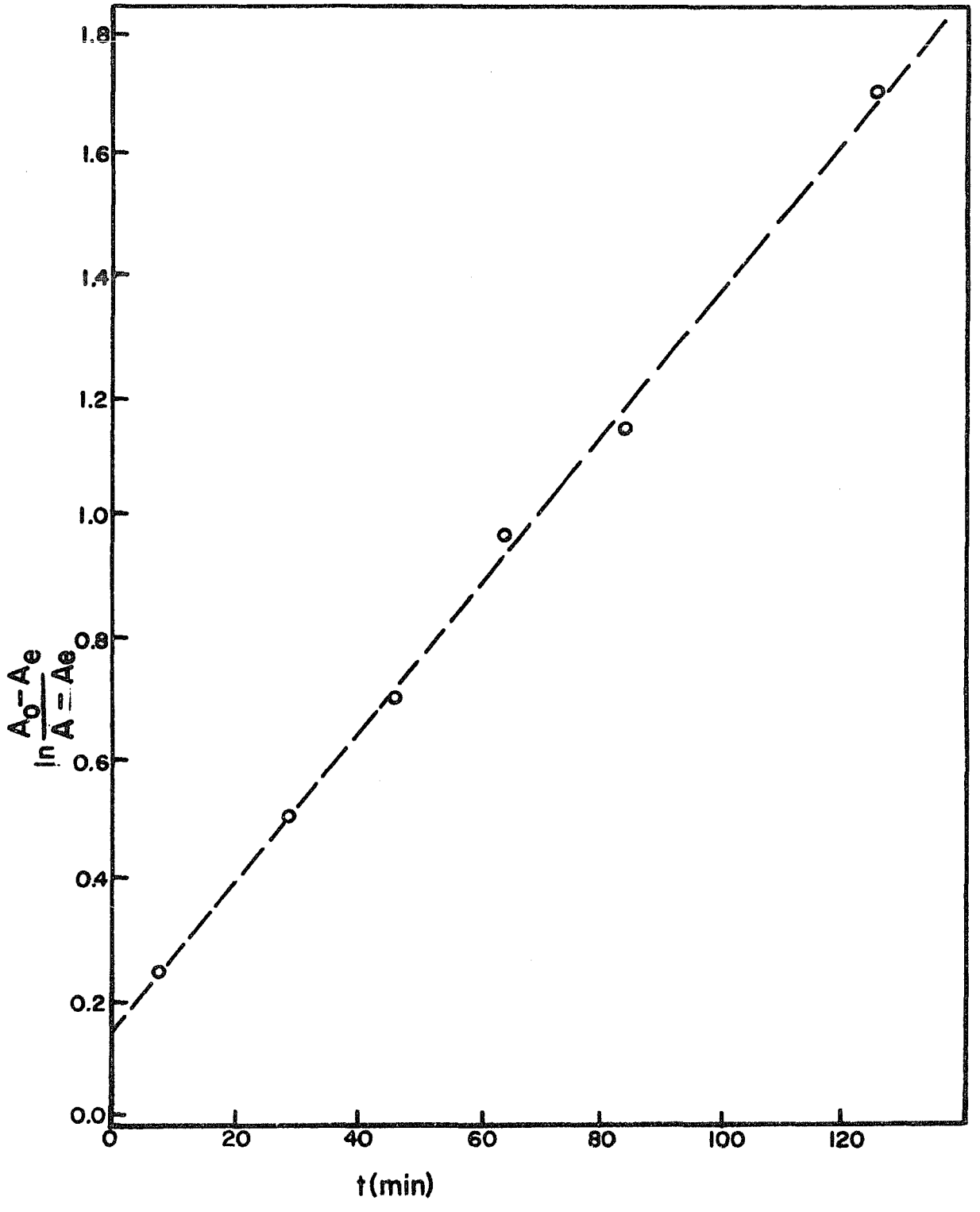


TABLE A-7

Isomerization of cis-1,2-Dimethyl-1-silacyclobutane (10a) with Potassium Cyanide[a] in DMF at 23°.

Run 1

Time, min	% 10a Remaining
6	90.1
20	88.9
42	87.7
62	86.8
82	85.5
103	84.6
128	83.5
156	82.6
181	81.8

[a]Relative concentration of 4.

TABLE A-7a

Rate Constants Derived from Table A-7.

Run	$k' \times 10^3$, min^{-1}	$k_1 \times 10^4$, sec^{-1}	r
1	1.20 ± 0.04	6.40 ± 0.20	0.995

FIGURE A-7. Isomerization of cis-1,2-Dimethyl-1-silacyclobutane with Potassium Cyanide. Data taken from Table A-7, run 1.

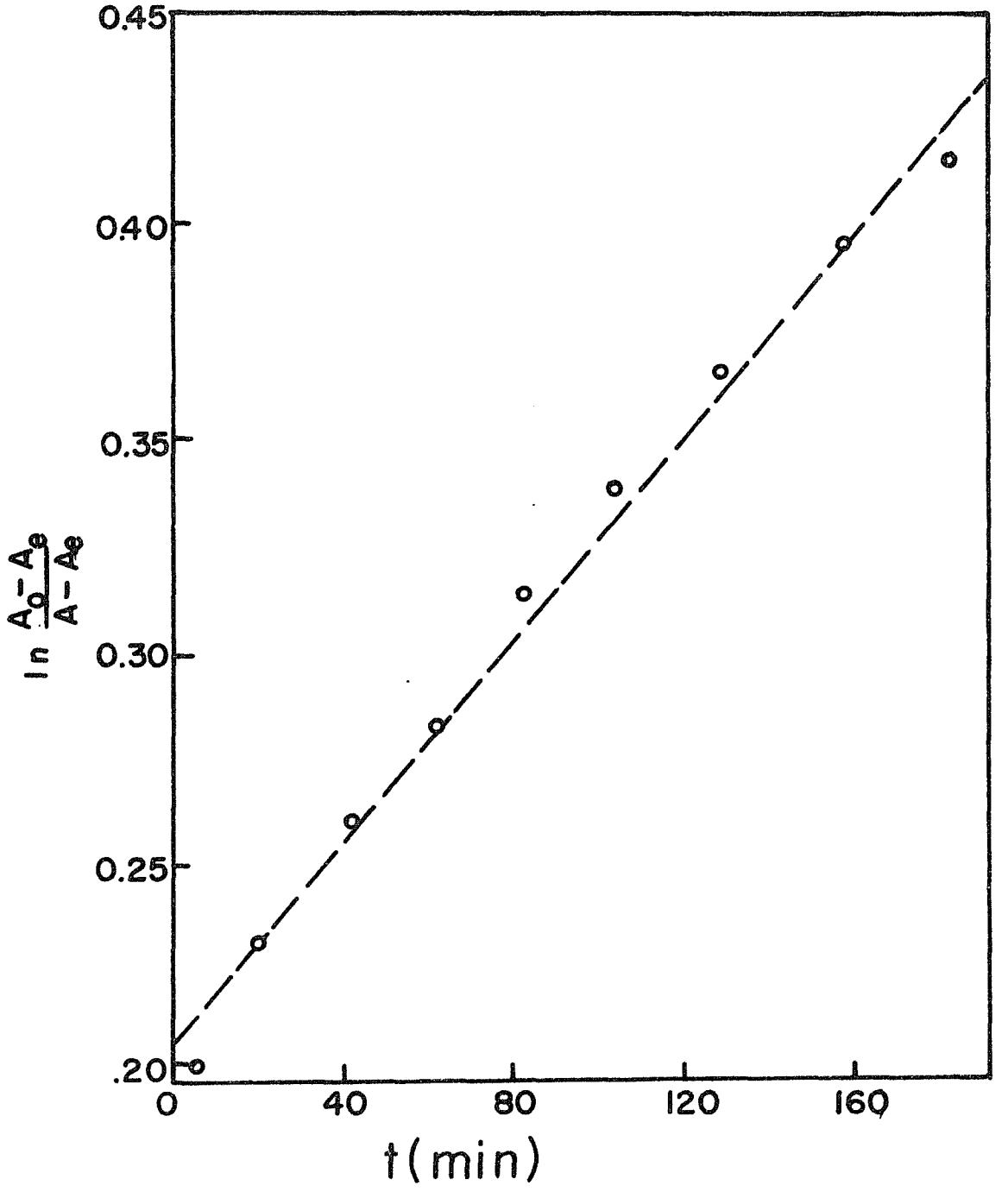


TABLE A-8

Isomerization of cis-1,2-Dimethyl-1-silacyclobutane (10a) with Potassium Cyanide[a] in DMF at 23°.

Run 1		Run 2	
Time, min	% 10a Remaining	Time, min	% 10a Remaining
6	90.3	6	92.8
27	86.9	27	90.1
51	85.6	54	88.3
74	83.6	74	87.2
115	81.2	98	86.0
136	80.0	115	85.0
158	79.4		
179	78.0		

Run 3	
Time, min	% 10a Remaining
7	95.4
32	94.9
49	94.2
72	94.0
100	93.8
160	92.7

[a]Relative concentration of 3.

TABLE A-8a

Rate Constants Derived from Table A-8.

Run	$k' \times 10^3$, min^{-1}	$k_1 \times 10^4$, min^{-1}	r
1	1.78 ± 0.16	9.53 ± 0.92	0.990
2	1.62 ± 0.20	8.63 ± 1.05	0.989
3	0.362 ± 0.044	1.94 ± 0.23	0.989

FIGURE A-8. Isomerization of cis-1,2-Dimethyl-1-silacyclobutane with Potassium Cyanide. Data taken from Table A-8, run 1.

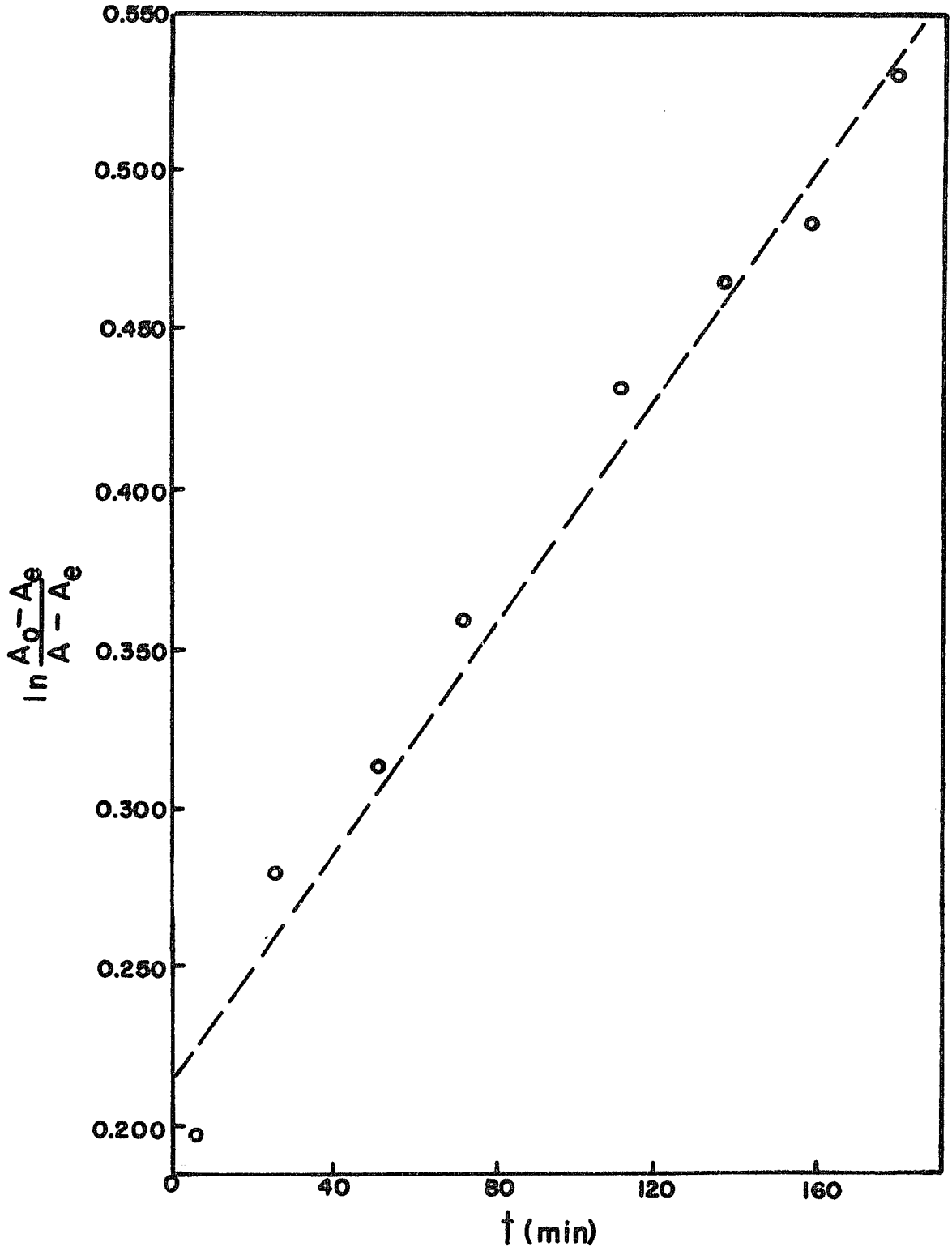


TABLE A-9

Isomerization of cis-1,2-Dimethyl-1-silacyclobutane (10a) with Potassium Cyanide[a] in DMF at 23°.

Run 1

Time, min	% 10a Remaining
23	94.9
55	94.1
76	93.9
109	93.3
131	93.1
156	92.6
184	92.2
219	91.7
245	90.5

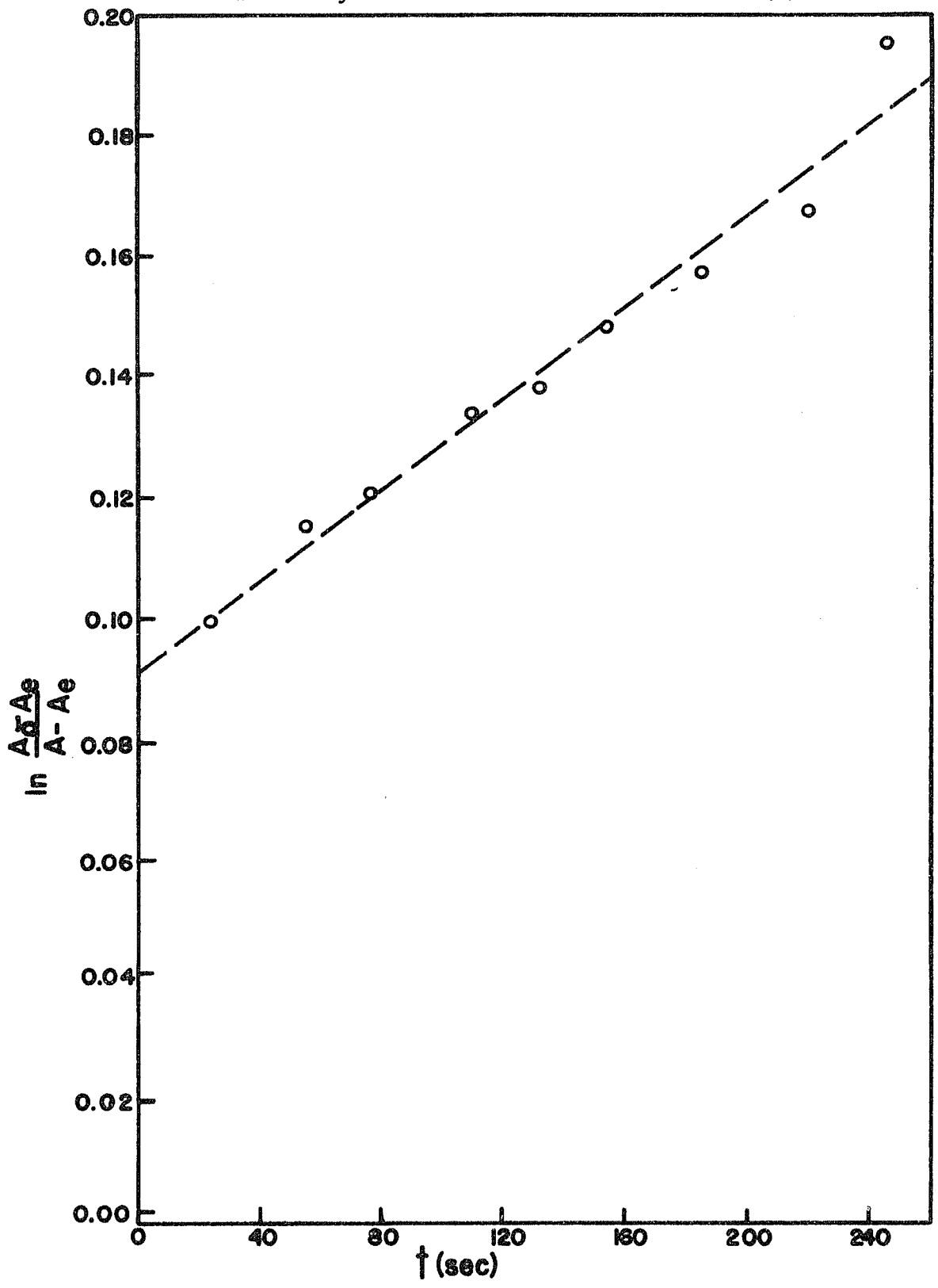
[a]Relative concentration of 2.

TABLE A-9a

Rate Constants Derived from Table A-9.

Run	$k' \times 10^4$, min^{-1}	$k_1 \times 10^4$, min^{-1}	r
1	3.81 ± 0.46	2.04 ± 0.24	0.983

FIGURE A-9. Isomerization of cis-1,2-Dimethyl-1-silacyclobutane with Potassium Cyanide. Data taken from Table A-9, run 1.



APPENDIX B

Specific Rate Data for Isomerization of 1-Chloro-1,2-dimethyl-1-silacyclobutane (described in Chapter IV)

TABLE B-1

Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane[a] (7a) with 2.0×10^{-3} M HMPT in CCl_4 at 45°.

Run 1			Run 1		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
15	125	41	25	128	38
35	123	48	40	112	43
60	115	58	55	111	45
80	108	60	71	111	53
105	100	64	97	106	59
122	98	65	112	102	63
140	93	71	129	103	62
174	93	70	145	98	67
195	93	75	161	98	69
211	92	78	183	94	71
235	89	78	200	92	72
255	88	80	220	94	74
			237	89	76
			253	93	76

[a] 0.75 M in 7. [b] From NMR.

TABLE B-1a

Rate Constants Derived from Table B-1.

Run	$k' \times 10^3$, sec^{-1}	$k_1 \times 10^3$, sec^{-1}	r
1	7.41 ± 0.51	3.85 ± 0.26	0.993
2	6.63 ± 0.53	3.45 ± 0.27	0.988

FIGURE B-1. Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane with 2.0 x 10^{-3} M HMPT. Data taken from Table B-1, run 1.

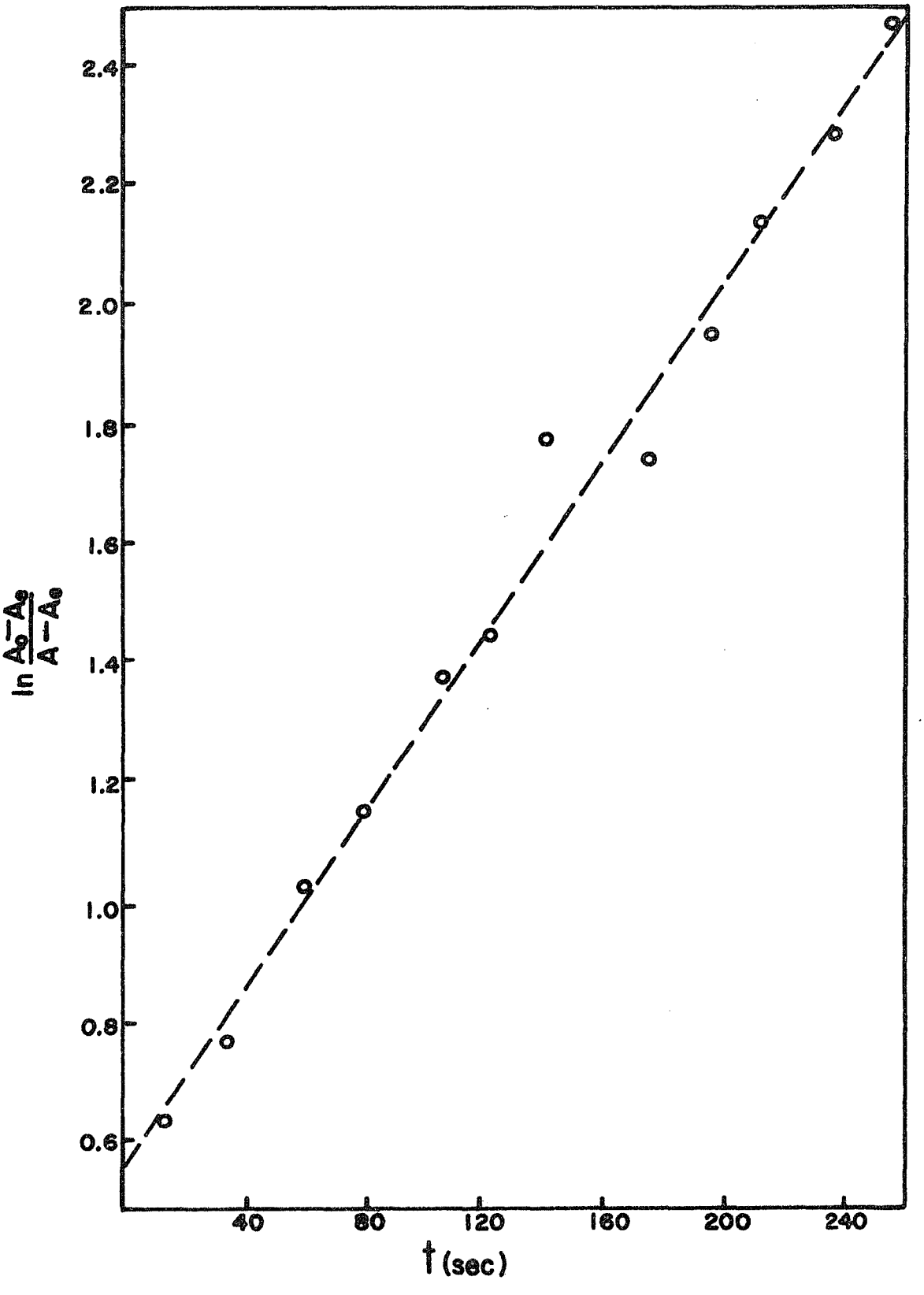


TABLE B-2

Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane[a] (7a) with 1.0×10^{-3} M HMPT in CCl_4 at 45°.

Run 1			Run 2		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7a		7a	7b
0	109	33	0	131	43
50	101	39	50	125	52
100	96	46	100	118	57
150	95	51	150	113	64
200	93	55	220	108	67
250	91	58	250	106	70
300	85	61	300	100	72
350	84	64	350	98	76
400	83	66	400	96	78
450	80	66	450	95	79

Run 3			Run 3 (continued)		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
0	137	38	210	115	66
30	129	42	240	110	66
60	125	46	270	108	69
90	124	50	400	103	77
120	120	55	450	101	78
150	118	58	500	99	79
180	120	63	550	99	83

[a] 0.75 M in 7. [b] From NMR.

TABLE B-2a

Rate Constants Derived from Table B-2.

Run	$k' \times 10^3$, sec^{-1}	$k_1 \times 10^3$, sec^{-1}	r
1	3.00 ± 0.12	1.56 ± 0.06	0.998
2	3.22 ± 0.13	1.67 ± 0.07	0.998
3	2.80 ± 0.09	1.45 ± 0.05	0.998

FIGURE B-2. Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane with 1.0×10^{-3} M HMPT. Data taken from Table B-2, run 2.

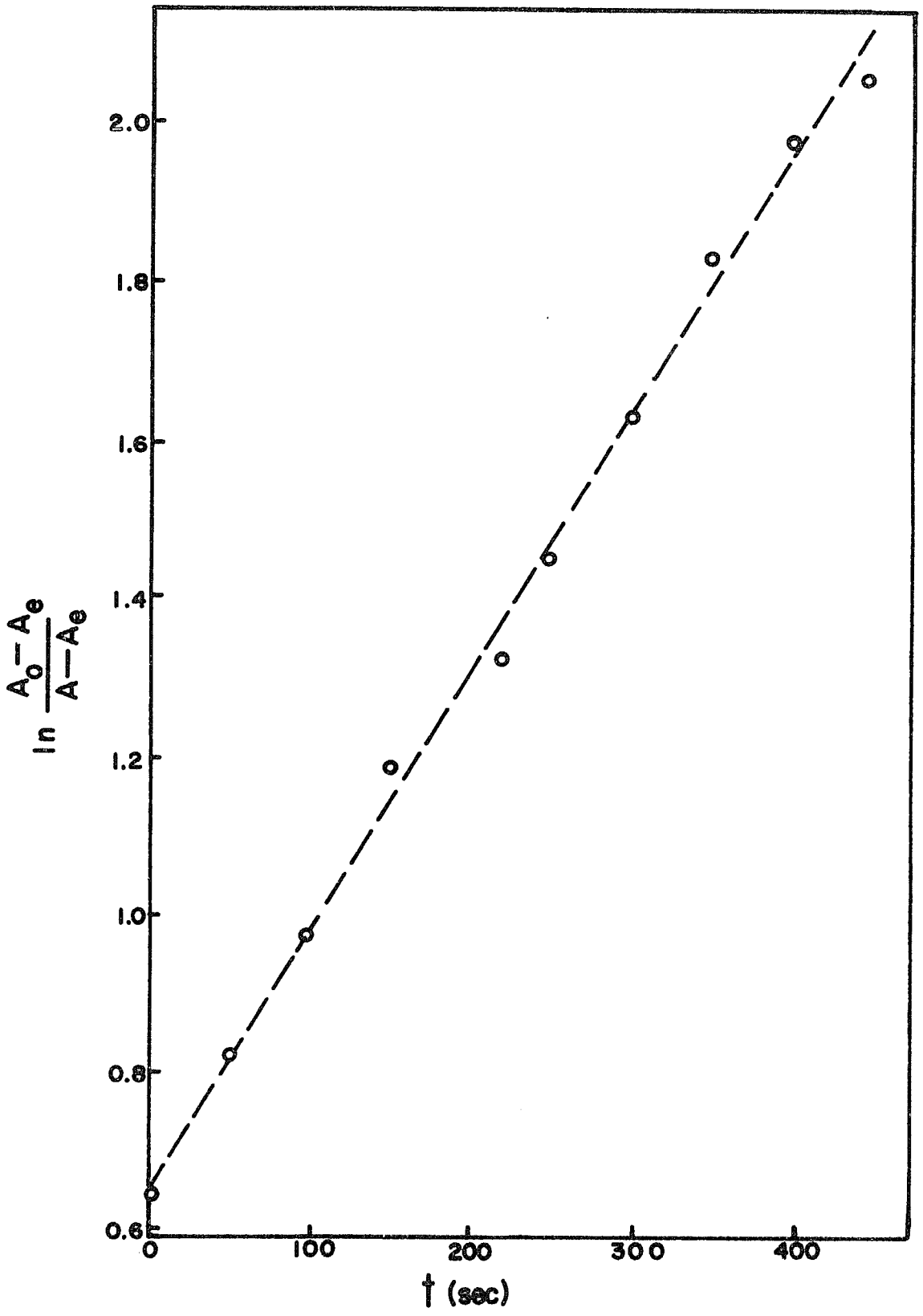


TABLE B-3

Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane[a] (7a) with 5.0×10^{-4} M HMPT in CCl_4 at 45°.

Run 1			Run 2		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
70	130	46	0	140	38
100	129	48	50	132	44
150	125	51	100	130	46
200	122	54	150	123	50
250	122	58	200	123	53
300	117	60	250	119	55
350	117	62	300	120	56
400	115	64	350	115	60
450	111	69	400	112	61
500	112	70	450	110	63
550	106	70	500	111	65
600	106	73	550	109	66
650	109	77	600	106	69
900	102	81	740	105	75
950	100	80	800	103	79
			850	102	79
			900	99	79
			950	99	81
			1000	98	82
			1050	98	81

TABLE B-3 (continued)

Run 3			Run 3 (continued)		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
0	105	32	450	87	55
50	104	36	500	83	57
100	101	39	550	85	57
150	101	42	600	82	58
200	96	44	650	81	59
300	91	49	700	80	61
350	89	52	750	80	61
400	88	53			

[a]0.75 M in 7. [b]From NMR.

TABLE B-3a

Rate Constants Derived from Table B-3.

Run	$k' \times 10^3$, sec^{-1}	$k_1 \times 10^4$, sec^{-1}	r
1	1.46 ± 0.04	7.58 ± 0.22	0.996
2	1.49 ± 0.05	7.76 ± 0.27	0.997
3	1.65 ± 0.08	8.56 ± 0.39	0.996

FIGURE B-3. Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane with 5.0×10^{-4} M HMPT. Data taken from Table B-3, run 2.

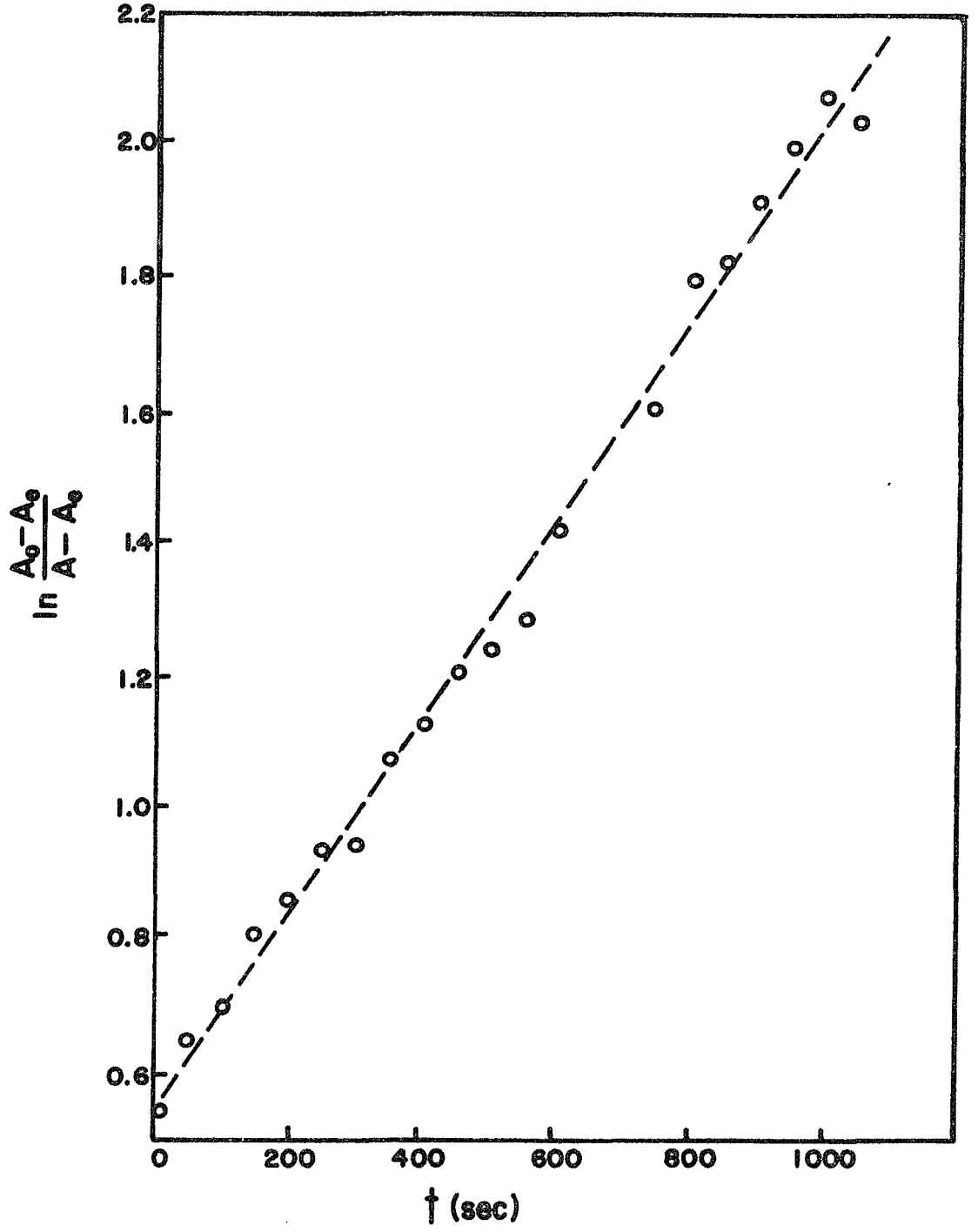


TABLE B-4

Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane (7a) with 2.5×10^{-4} M HMPT in CCl_4 at 45°.

Run 1			Run 2		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
0	111	26	0	139	29
25	143	34	50	138	32
100	138	37	100	139	34
200	133	41	150	134	35
300	131	46	200	136	37
400	129	47	300	132	40
500	128	48	400	129	42
600	128	54	500	128	44
700	122	56	600	122	48
800	124	60	700	126	48
900	119	61	800	117	50
1000	118	63	900	119	55
1100	118	63	1000	117	57
1200	121	64	1100	116	58
1400	120	69	1200	111	57
1500	112	70	1300	106	61
1600	106	73	1400	107	64
1700	109	72	1500	105	66
1800	104	79	1700	101	67
2000	105	79	1900	103	70
2100	101	78	2000	103	69
2200	103	82	2100	105	71
2300	100	81	2200	103	72

[a] 0.75 M in 7. [b] From NMR.

TABLE B-4a

Rate Constants Derived from Table B-4.

Run	$k' \times 10^4$, sec^{-1}	$k_1 \times 10^4$, sec^{-1}	r
1	6.47 ± 0.34	3.36 ± 0.17	0.991
2	5.56 ± 0.29	2.89 ± 0.15	0.992

FIGURE B-4. Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane with 2.5×10^{-4} M HMPT. Data taken from Table B-4, run 2.

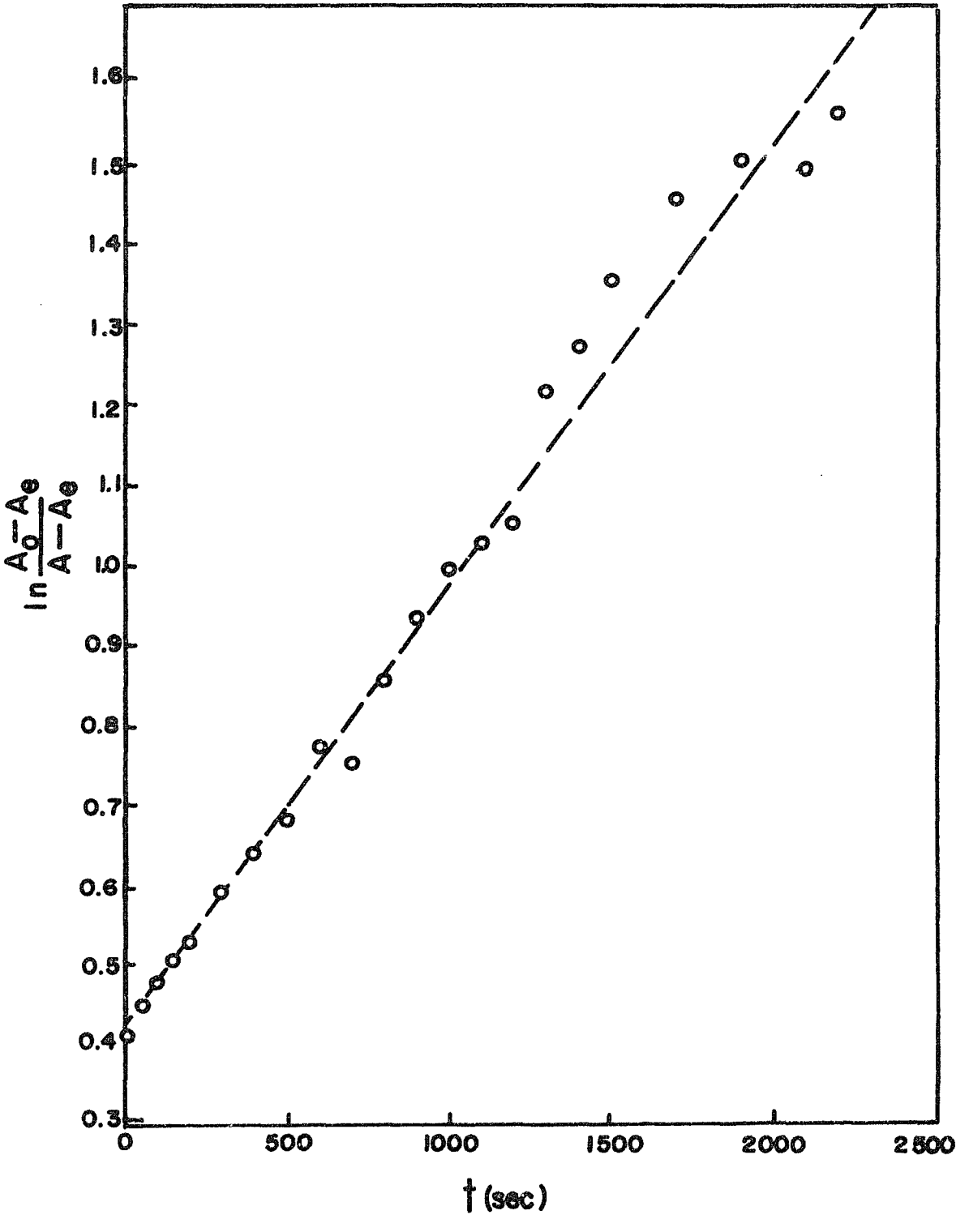


TABLE B-5

Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane (7a) with 1.0×10^{-4} M HMPT in CCl_4 at 45°.

Run 1			Run 2		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
60	143	34	660	119	30
150	140	36	720	116	31
200	143	36	900	115	33
300	140	38	1080	110	34
400	139	38	1260	110	35
500	136	39	1440	112	36
700	132	43	1500	110	38
800	133	43	1620	104	38
900	132	46	2340	99	43
1000	129	46	2520	101	48
1100	132	45	2580	100	45
1300	130	49	2760	100	47
1500	128	49	2880	97	50
1600	130	50	3060	95	48
1700	127	54	3240	94	49
1800	126	53	3420	95	51
1900	128	51	3600	95	51
2000	121	49	3780	93	50
2100	117	53	3960	91	52
2200	124	58	4140	91	53
2600	123	57			
2800	124	62			
3050	117	61			
3200	122	63			
3400	120	67			
3600	111	65			

TABLE B-5 (continued)

Run 1 (continued)		
Time, sec	Relative Area[b]	
	7a	7b
3800	112	68
4000	108	68
4200	105	69
4400	105	70
4600	107	71
4800	103	71
5000	107	72

[a]0.75 M in 7. [b]From NMR.

TABLE B-5a

Rate Constants Derived from Table B-5.

Run	$k' \times 10^4$, sec^{-1}	$k_1 \times 10^4$, sec^{-1}	r
1	2.17 ± 0.09	1.13 ± 0.05	0.992
2	2.14 ± 0.12	1.11 ± 0.06	0.992

FIGURE B-5. Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane with 1.0×10^{-4} M HMPT. Data taken from Table B-5, run 1.

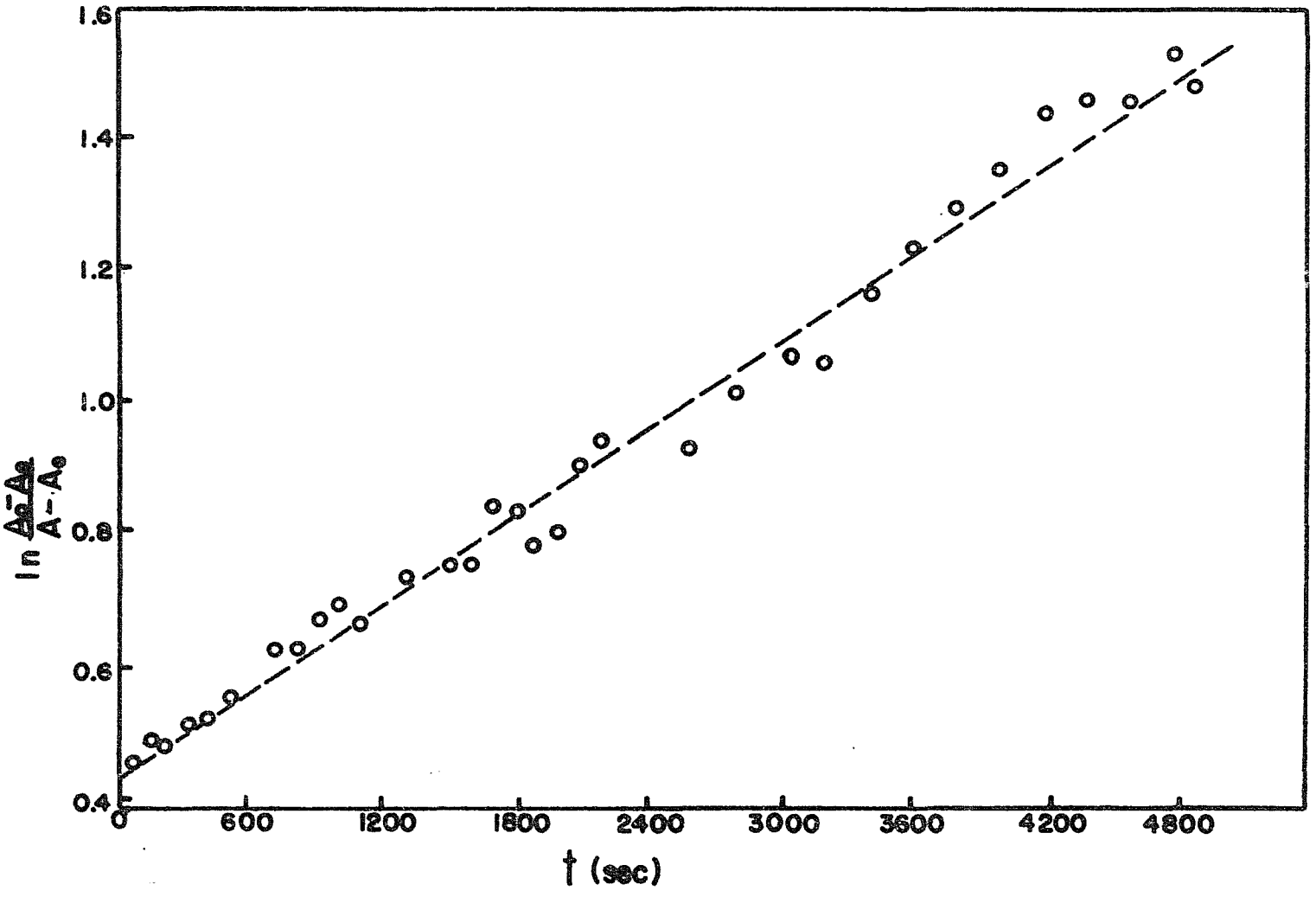


TABLE B-6

Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane[a] (7a) with 5.0×10^{-5} M HMPT in CCl_4 at 45°.

Run 1			Run 2		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
0	154	28	0	150	28
25	150	27	50	148	29
100	152	28	100	148	29
200	150	26	150	147	30
300	150	29	225	148	30
400	147	28	300	145	30
500	146	29	400	146	31
600	148	30	500	149	31
700	142	31	600	145	32
800	145	31	700	145	32
900	144	32	800	143	32
1000	144	32	900	143	34
1120	142	33	1100	138	35
1200	144	33	1200	141	36
1300	141	34	1300	137	37
1400	142	34	1400	141	37
1500	139	34	1500	139	38
1600	140	36	1600	137	38
1700	138	36	1700	141	38
1800	141	37	1800	140	40
1900	139	37	1825	142	40
2000	138	37	1900	142	40
2100	138	37	2000	142	41
2200	136	38	2100	141	39
2300	139	39	2200	138	42
2400	139	38	2300	138	42
2500	134	38	2400	137	43

TABLE B-6 (continued)

Run 1 (continued)			Run 2 (continued)		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
2600	140	38	2500	133	40
2900	138	39	2600	138	43
3000	142	41	2700	136	44
3100	133	39	2800	134	44
3200	135	40	2900	134	44
3300	135	42	3000	136	45
3400	132	44	3200	135	46
3500	132	43	3300	137	46
3700	131	44	3400	137	48
3800	130	44	3500	137	47
4000	127	44	3600	134	47
4200	126	46	3700	134	48
4300	129	45	3800	134	49
4400	127	47	3900	131	49
4500	135	47	4000	126	49
4600	132	49	4100	126	50
4700	130	47	4200	131	50
4800	131	47	4300	128	52
4900	132	48	4400	127	52
5000	130	48	4500	125	52
5100	128	49	4600	130	51
5200	130	50	4700	128	52
5300	131	50	4800	125	53
5400	131	49			
5500	130	51			
5600	130	50			
5700	129	51			
5800	128	52			
5900	129	51			

TABLE B-6 (continued)

Run 3			Run 3 (continued)		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
270	128	23	3120	116	37
360	128	23	3420	117	35
480	128	24	3720	116	36
600	125	25	3900	113	37
720	124	24	4380	108	37
840	124	26	4500	112	38
960	126	27	4740	112	40
1140	118	26	4800	111	39
1320	119	28	5040	108	40
1500	117	28	5100	109	39
1680	122	28	5340	109	40
1920	119	29	5400	105	41
2160	114	30	5640	109	42
2400	117	32	5700	109	41
2640	115	33	5940	105	41
2880	113	33	6000	110	43

[a]0.75 M in 7. [b]From NMR.

TABLE B-6a

Rate Constants Derived from Table B-6.

Run	$k' \times 10^5$, sec^{-1}	$k_1 \times 10^5$, sec^{-1}	r
1	7.73 ± 0.25	4.02 ± 0.13	0.992
2	9.57 ± 0.31	4.98 ± 0.16	0.993
3	7.54 ± 0.30	3.92 ± 0.15	0.993

FIGURE B-6. Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane with 5.0×10^{-5} M HMPT. Data taken from Table B-6, run 2.

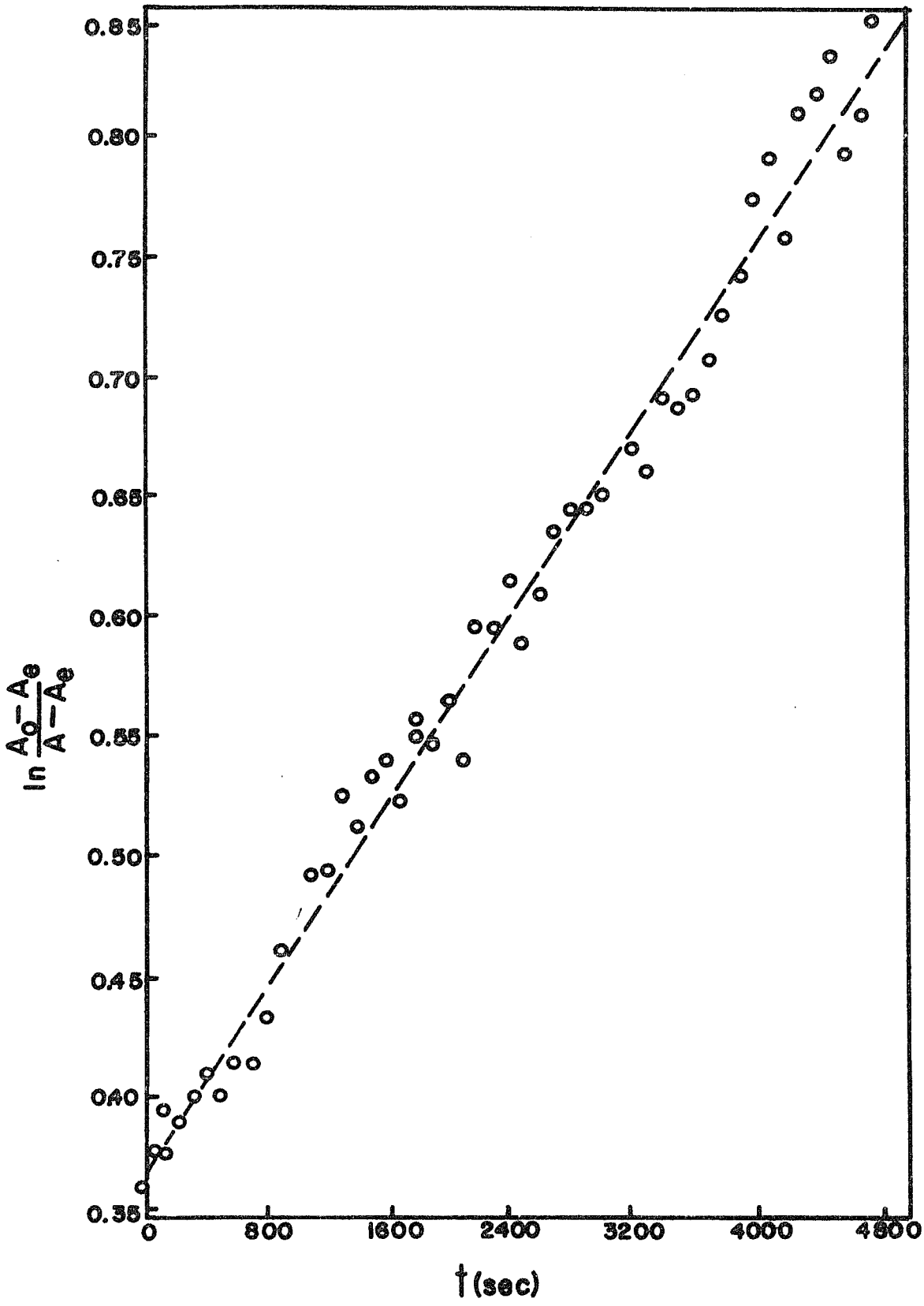


TABLE B-7

Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane (7a) with 2.5×10^{-5} M HMPT in CCl_4 at 45°.

Run 1			Run 1 (continued)		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
0	154	27	3600	143	34
100	150	27	3800	144	34
200	151	28	4000	144	36
400	151	28	4200	139	35
600	146	29	4400	144	36
800	152	28	4600	140	37
900	148	29	4800	144	36
1000	150	29	5000	145	38
1200	153	29	5200	144	37
1300	149	30	5400	140	36
1400	148	30	5600	143	38
1600	146	31	5800	144	40
1800	150	30	6000	138	38
1900	146	30	6200	141	39
2000	153	30	6400	140	40
2200	144	32	6600	137	40
2400	148	32	6800	138	40
2600	150	33	7000	141	40
2800	147	33	7200	137	42
3000	141	34	7400	141	41
3200	148	34	7600	141	42
3300	144	34	7800	142	43
3400	145	35	8000	146	42

TABLE B-7 (continued)

Run 1 (continued)			Run 1 (continued)		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
8200	143	43	10200	138	45
8400	143	43	10600	134	45
8600	136	43	10800	137	44
8800	140	43	11000	137	46
9000	140	43	11200	137	47
9200	145	44	11400	137	47
9400	135	44	11600	136	47
9600	140	44	11800	136	48
9800	141	44	12000	136	48

[a]0.75 M in 7. [b]From NMR.

TABLE B-7a

Rate Constants Derived from Table B-7.

Run	$k' \times 10^5$, sec^{-1}	$k_1 \times 10^5$, sec^{-1}	r
1	2.93 ± 0.14	1.52 ± 0.07	0.981

FIGURE B-7. Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane with 2.5×10^{-5} M HMPT. Data taken from Table B-7, run 1.

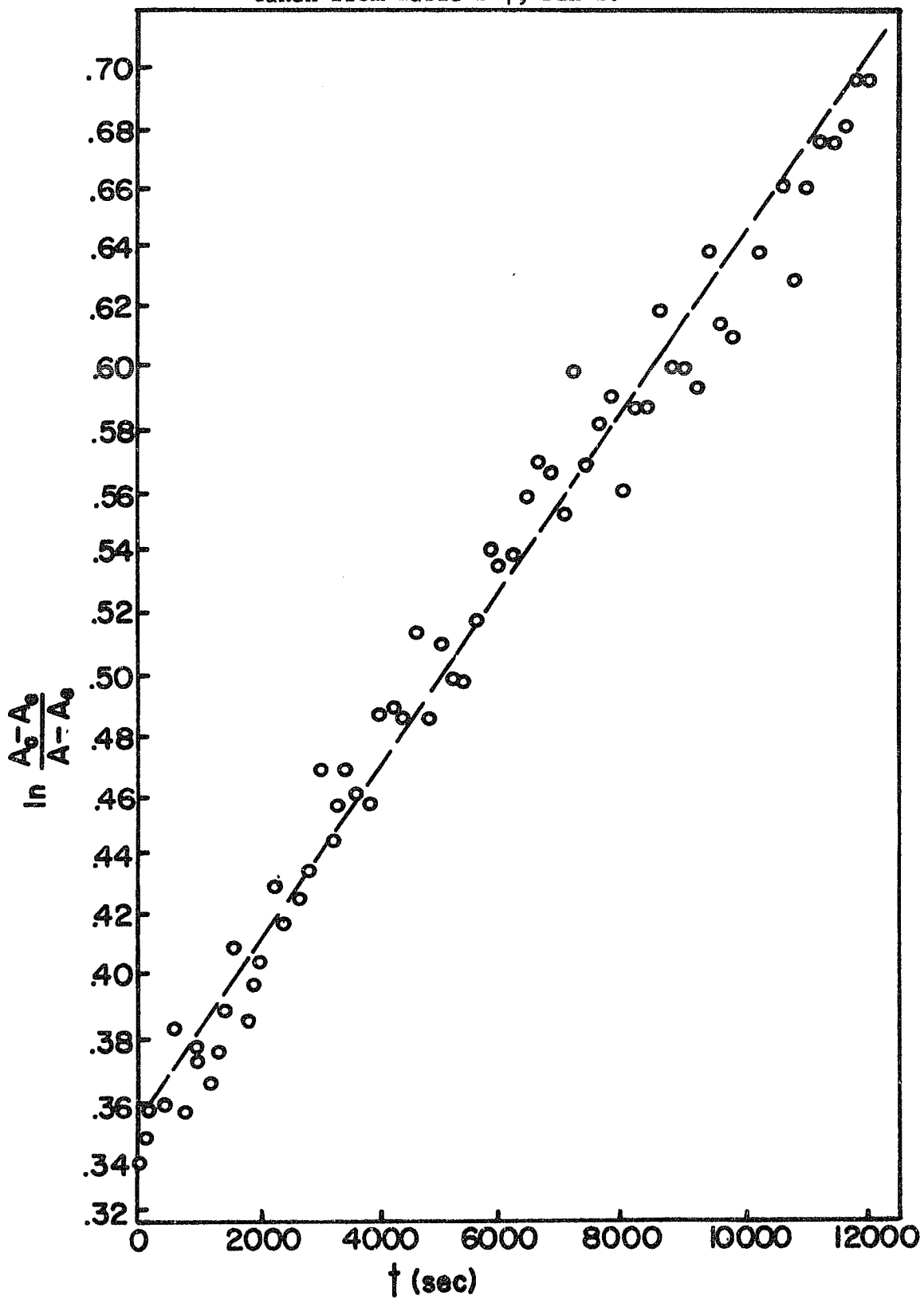


TABLE B-8

Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane[a] (7a) with 5.0×10^{-4} M HMPT in CCl_4 at 45°.

Run 1			Run 2		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
0	110	32	0	116	30
30	108	36	25	111	34
64	108	36	50	111	37
90	111	36	80	109	36
150	100	41	110	107	40
180	104	41	140	108	43
210	98	45	170	105	43
231	96	43	200	103	46
260	98	45	230	97	48
290	97	48	260	98	47
320	90	48	290	99	49
350	93	50	320	96	53
390	95	54	350	94	55
420	89	56	380	90	53
450	86	50	410	96	56
480	88	48	440	91	61
650	81	61	530	90	61
680	80	56	590	91	68
710	86	63	620	84	67
740	85	60	650	86	70
770	82	67			
800	76	60			

[a] 1.13 M in 7. [b] From NMR.

TABLE B-8a

Rate Constants Derived from Table B-8.

Run	$k' \times 10^3$, sec^{-1}	$k_1 \times 10^4$, sec^{-1}	r
1	1.63 ± 0.15	8.47 ± 0.78	0.977
2	2.13 ± 0.15	11.1 ± 0.8	0.988

FIGURE B-8. Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane with 5.0×10^{-4} M HMPT. Data taken from Table B-8, run 2.

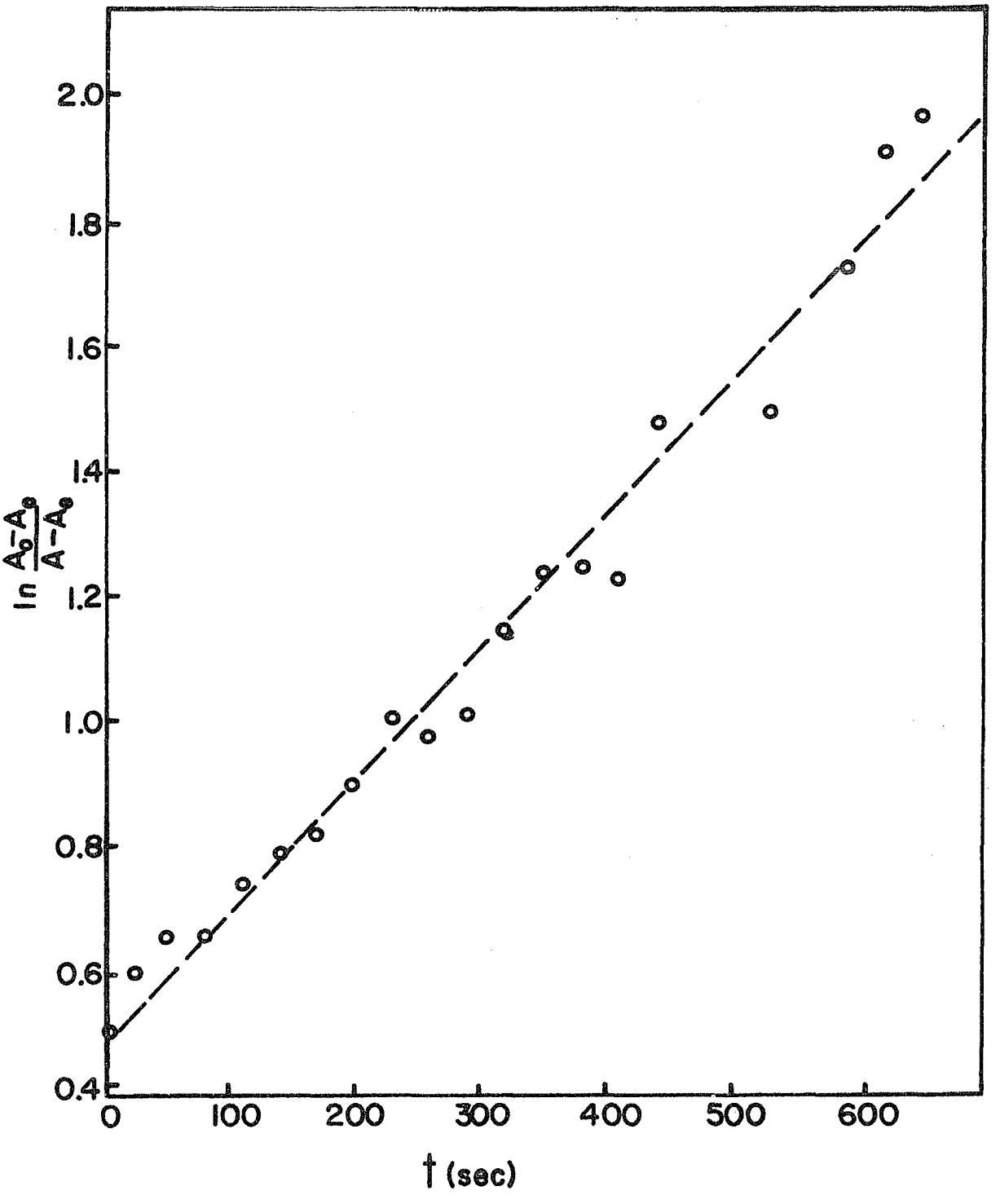


TABLE B-9

Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane[a] (7a) with 1.0×10^{-3} M HMPT in CCl_4 at 45°.

Run 1			Run 2		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
0	80	25	0	91	24
30	82	24	30	84	27
60	85	30	60	85	30
90	80	33	90	82	32
120	76	35	120	83	33
150	76	33	150	80	38
180	75	38	180	78	35
210	78	40	210	78	40
240	71	40	240	76	39
270	70	42	270	75	44
300	69	45	300	70	43
330	67	50	330	67	45
360	69	49	360	71	43
390	65	51	390	67	43
420	64	48	420	67	48
450	66	48	450	64	44
480	66	49	480	68	50
			510	64	50

[a] 0.30 M in 7. [b] From NMR.

TABLE B-9a

Rate Constants Derived from Table B-9.

Run	$k' \times 10^3$, sec^{-1}	$k_1 \times 10^3$, sec^{-1}	r
1	2.78 ± 0.35	1.44 ± 0.18	0.966
2	2.42 ± 0.20	1.26 ± 0.10	0.984

FIGURE B-9. Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane with 1.0×10^{-3} M HMPT. Data taken from Table B-9, run 2.

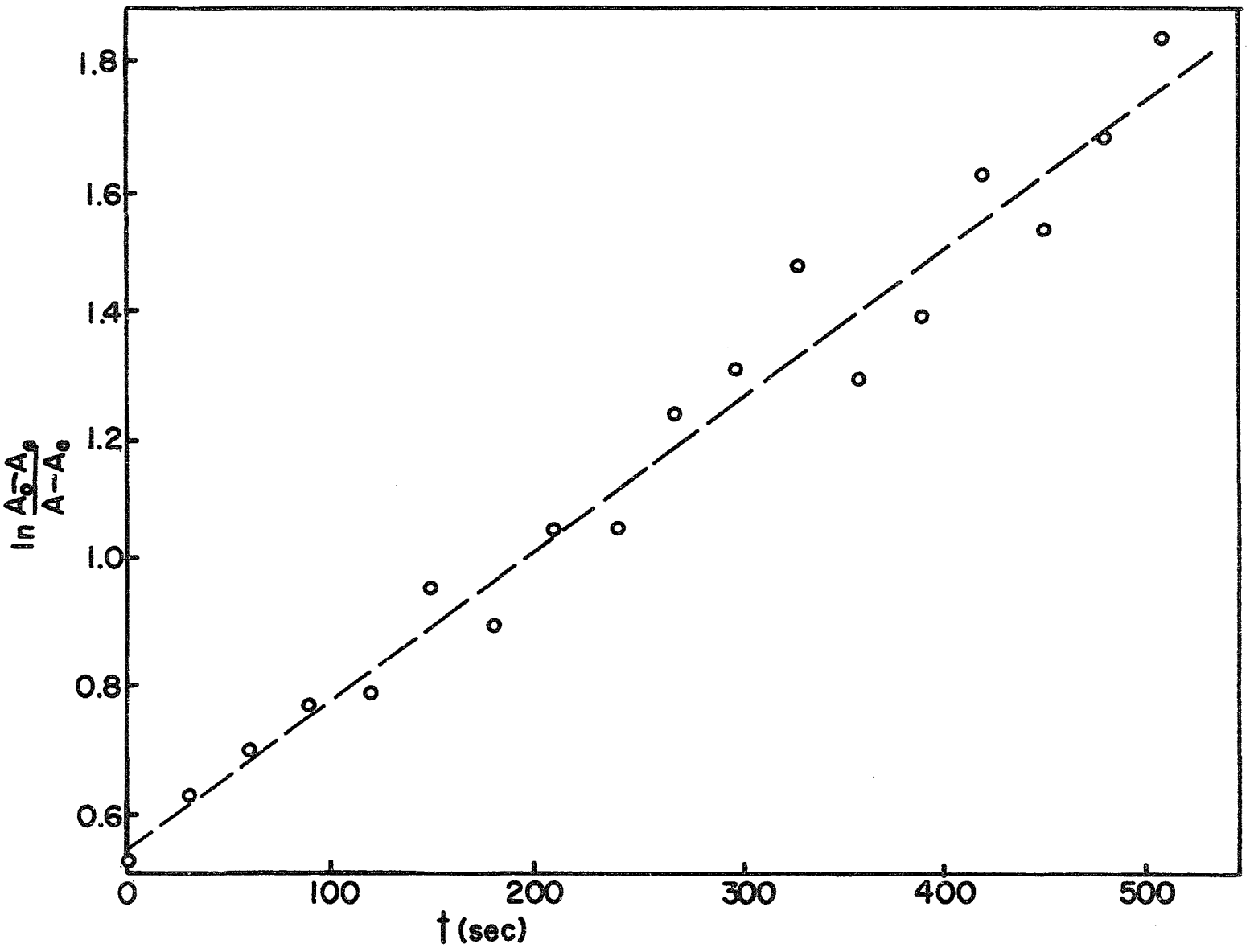


TABLE B-10

Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane[a] (7a) with 5.0×10^{-4} M HMPT in CCl_4 at 45°.

Run 1			Run 2		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
0	99	24	0	115	26
50	94	25	30	110	30
100	94	29	60	116	31
150	95	33	90	112	33
200	93	36	180	115	37
250	97	35	240	102	40
300	86	38	300	104	36
350	87	41	360	103	48
400	84	40	420	96	49
450	85	41	480	95	47
500	83	48	540	94	50
550	80	46	600	94	56
600	83	47	720	93	59
650	87	46	900	85	59
700	77	49			
750	74	52			
800	84	52			
850	77	53			
900	71	55			
950	75	55			

[a] 0.30 M in 7. [b] From NMR.

TABLE B-10a

Rate Constants Derived from Table B-10.

Run	$k' \times 10^3$, sec^{-1}	$k_1 \times 10^4$, sec^{-1}	r
1	1.29 ± 0.14	6.71 ± 0.71	0.971
2	1.26 ± 0.11	6.50 ± 0.56	0.987

FIGURE B-10. Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclubutane with 5.0×10^{-4} M HMPT. Data taken from Table B-10, run 1.

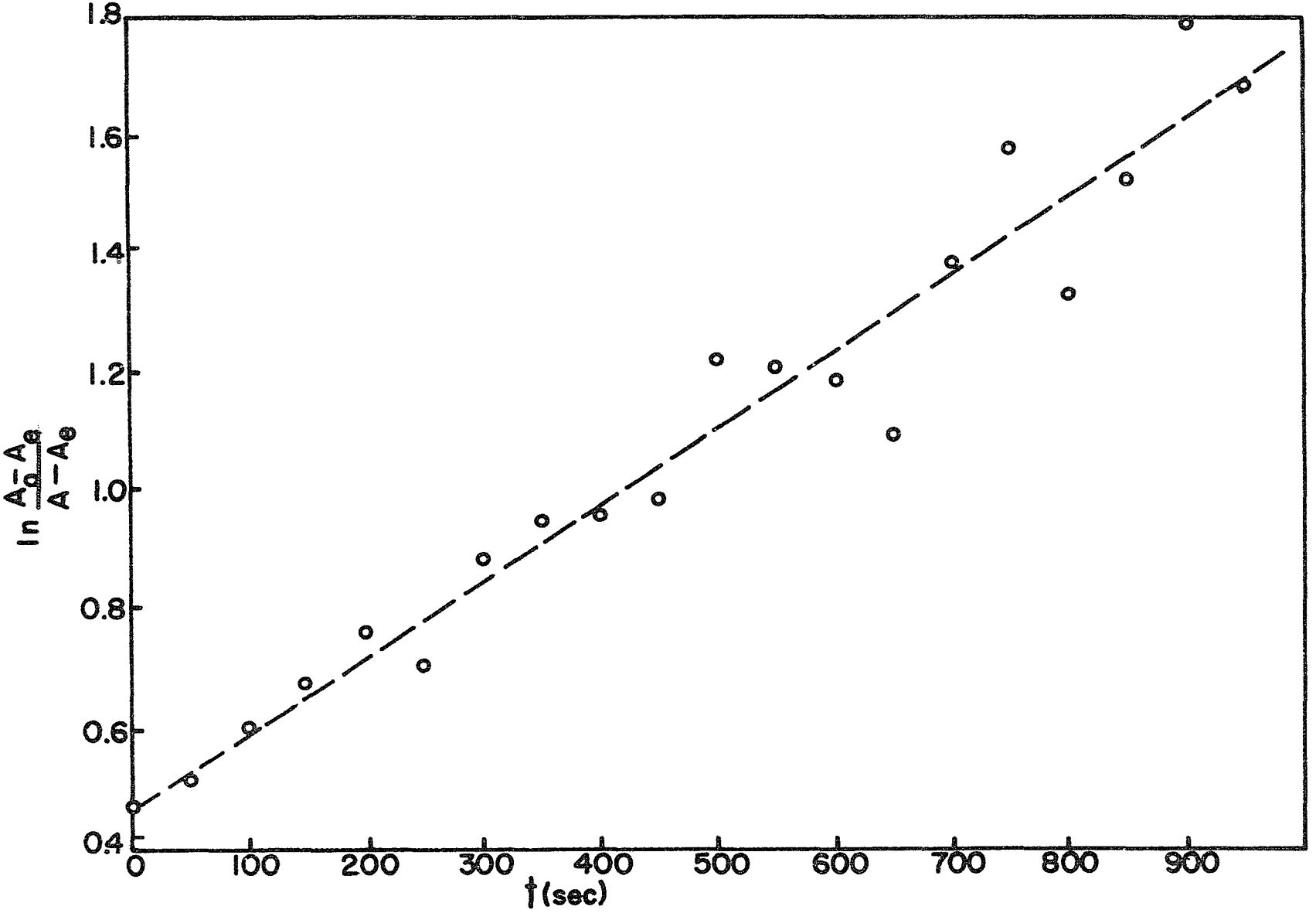


TABLE B-11

Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane[a] (7a) with 2.5×10^{-4} M HMPT in CCl_4 at 45°.

Run 1			Run 1 (continued)		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
0	91	20	930	75	35
30	94	21	960	75	36
60	89	21	1020	80	37
120	90	23	1080	72	38
180	89	25	1140	77	35
240	91	25	1200	80	36
300	84	24	1260	74	42
360	87	27	1320	70	40
390	86	30	1380	73	40
420	86	30	1440	73	40
480	83	29	1500	71	40
540	83	28	1560	72	41
600	83	32	1620	75	43
660	80	33	1680	68	40
720	81	32	1740	68	42
780	80	37	1800	70	43
840	81	33			

[a] 0.30 M in 7. [b] From NMR.

TABLE B-11a

Rate Constants Derived from Table B-11.

Run	$k' \times 10^4$, sec^{-1}	$k_1 \times 10^4$, sec^{-1}	r
1	4.98 ± 0.34	2.58 ± 0.17	0.980

FIGURE B-11. Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane with 2.5×10^{-4} M HMPT. Data taken from Table B-11, run 1.

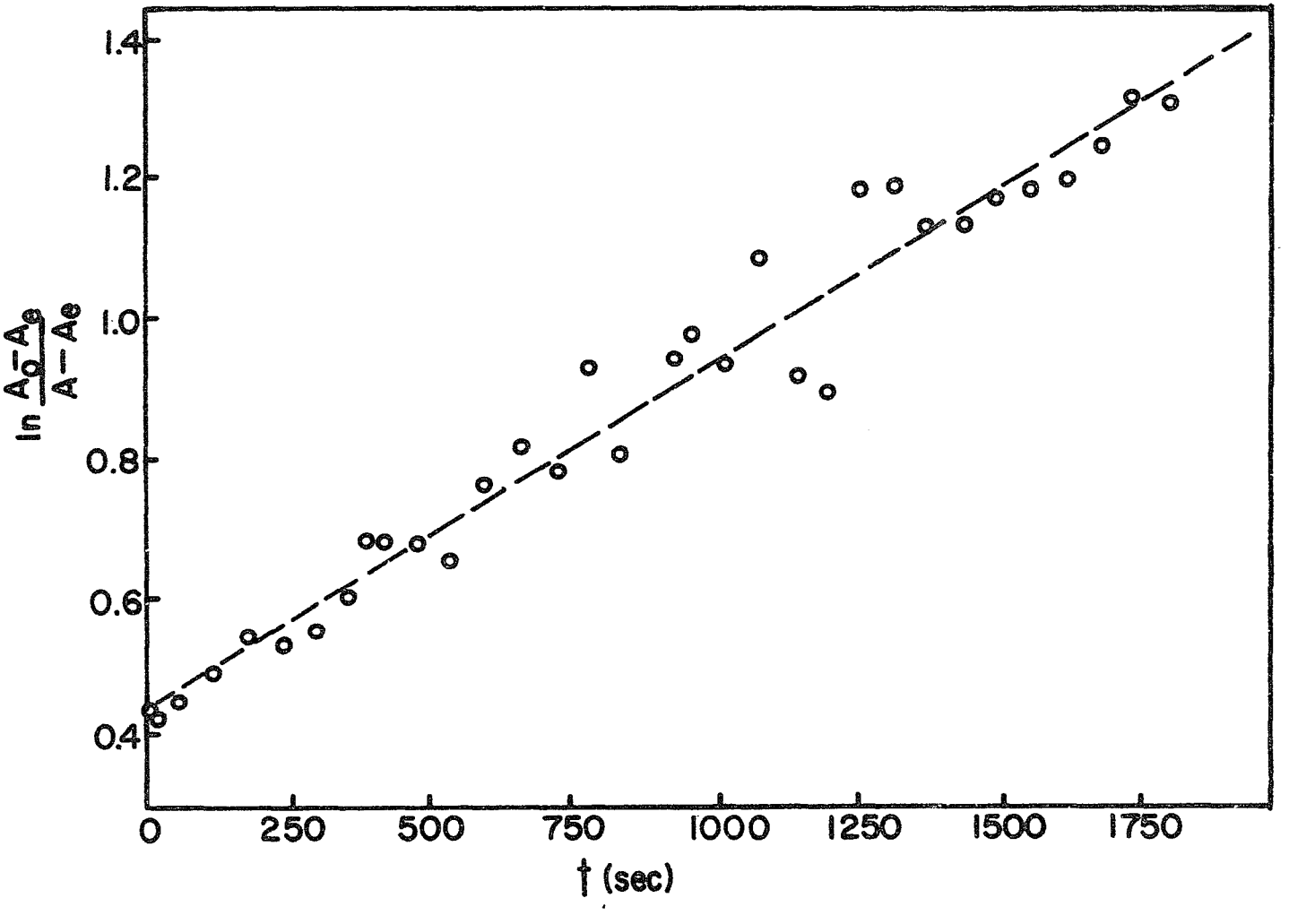


TABLE B-12

Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane[a] (7a) with 1.0×10^{-4} M HMPT in CCl_4 at 45°.

Run 1			Run 1 (continued)		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
20	93	21	1680	89	33
50	94	22	1800	82	34
70	96	21	1920	82	34
120	93	23	2040	83	33
150	91	24	2160	78	33
180	93	23	2280	82	38
240	96	23	2400	77	36
300	89	24	2520	78	40
360	95	25	2640	79	41
420	90	24	2760	79	39
480	93	23	2880	74	40
540	95	24	3000	78	40
600	89	21	3120	76	41
720	94	26	3240	75	44
750	83	28	3360	72	42
780	85	26	3480	71	40
840	89	28	3600	74	41
900	89	28	3840	75	44
960	89	28	3960	76	47
1080	88	28	4080	73	43
1200	83	29	4200	74	46
1440	88	33	4320	75	46
1500	84	30	4440	72	47
1560	85	31			

[a] 0.30 M in 7. [b] From NMR.

TABLE B-12a

Rate Constants Derived from Table B-12.

Run	$k' \times 10^4$, sec^{-1}	$k_1 \times 10^4$, sec^{-1}	r
1	2.20 ± 0.09	1.14 ± 0.05	0.989

FIGURE B-12. Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane with 1.0×10^{-4} M HMPT. Data taken from Table B-12, run 1.

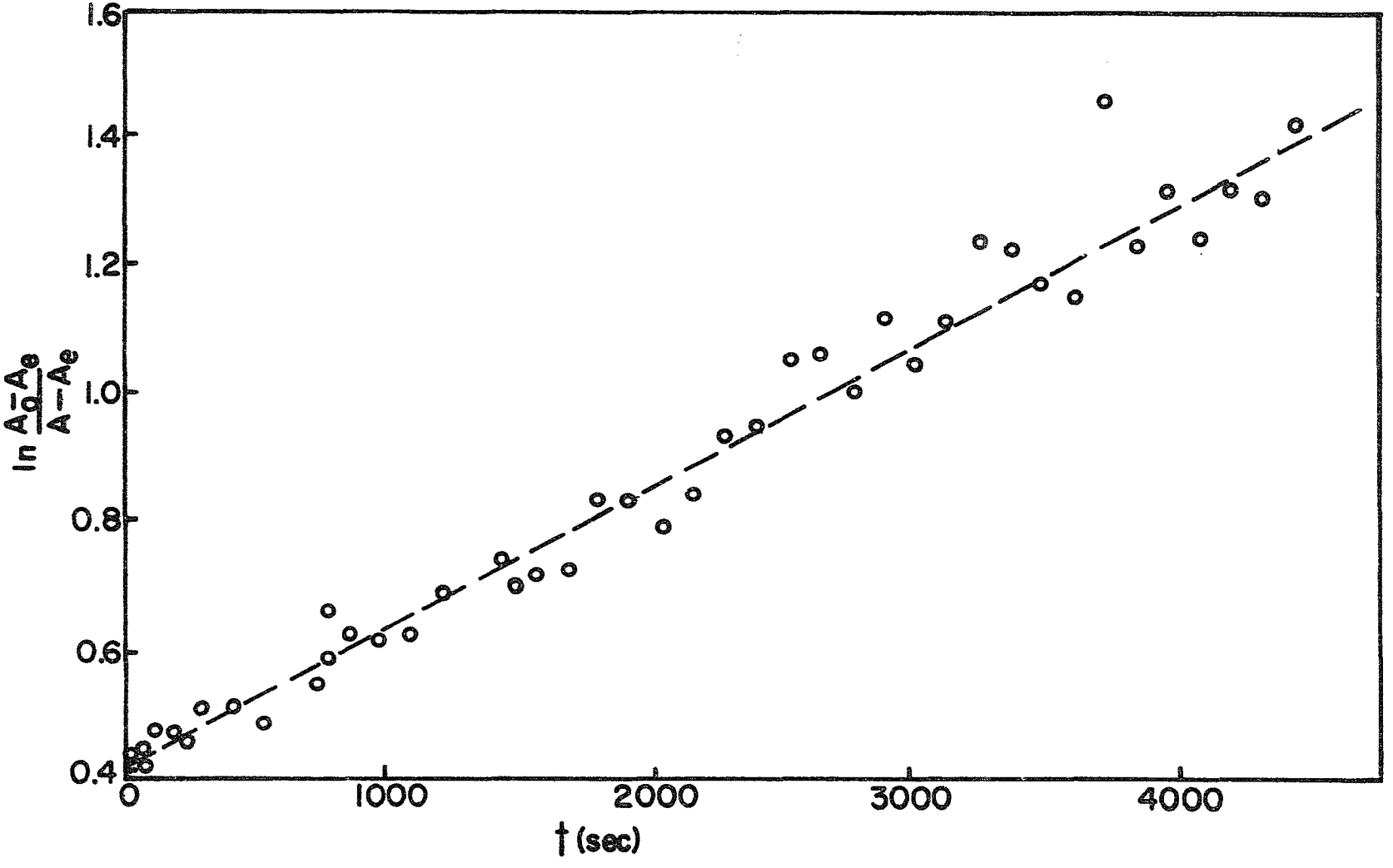


TABLE B-13

Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane[a] (7a) with 5.0×10^{-4} M HMPT in CCl_4 at 329°K.

Run 1			Run 2		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
0	113	31	0	110	40
50	108	34	25	105	40
100	105	39	55	105	45
150	102	44	100	109	45
200	100	45	150	92	48
250	101	48	218	98	54
300	93	50	250	97	56
350	92	56	300	93	56
410	93	56	350	95	58
450	94	55	400	90	63
504	92	61	450	92	64
550	90	62	500	90	63
600	85	60	550	90	65
650	85	61	600	89	65
700	81	64	700	83	68
750	88	67	750	83	66

[a] 0.75 M in 7. [b] From NMR.

TABLE B-13a

Rate Constants Derived from Table B-13.

Run	$k' \times 10^3$, sec^{-1}	$k_1 \times 10^4$, sec^{-1}	r
1	1.72 ± 0.13	8.94 ± 0.68	0.989
2	1.66 ± 0.14	8.63 ± 0.73	0.985

FIGURE B-13. Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane with 5.0×10^{-4} M HMPT at 329°K. Data taken from Table B-13, run 1.

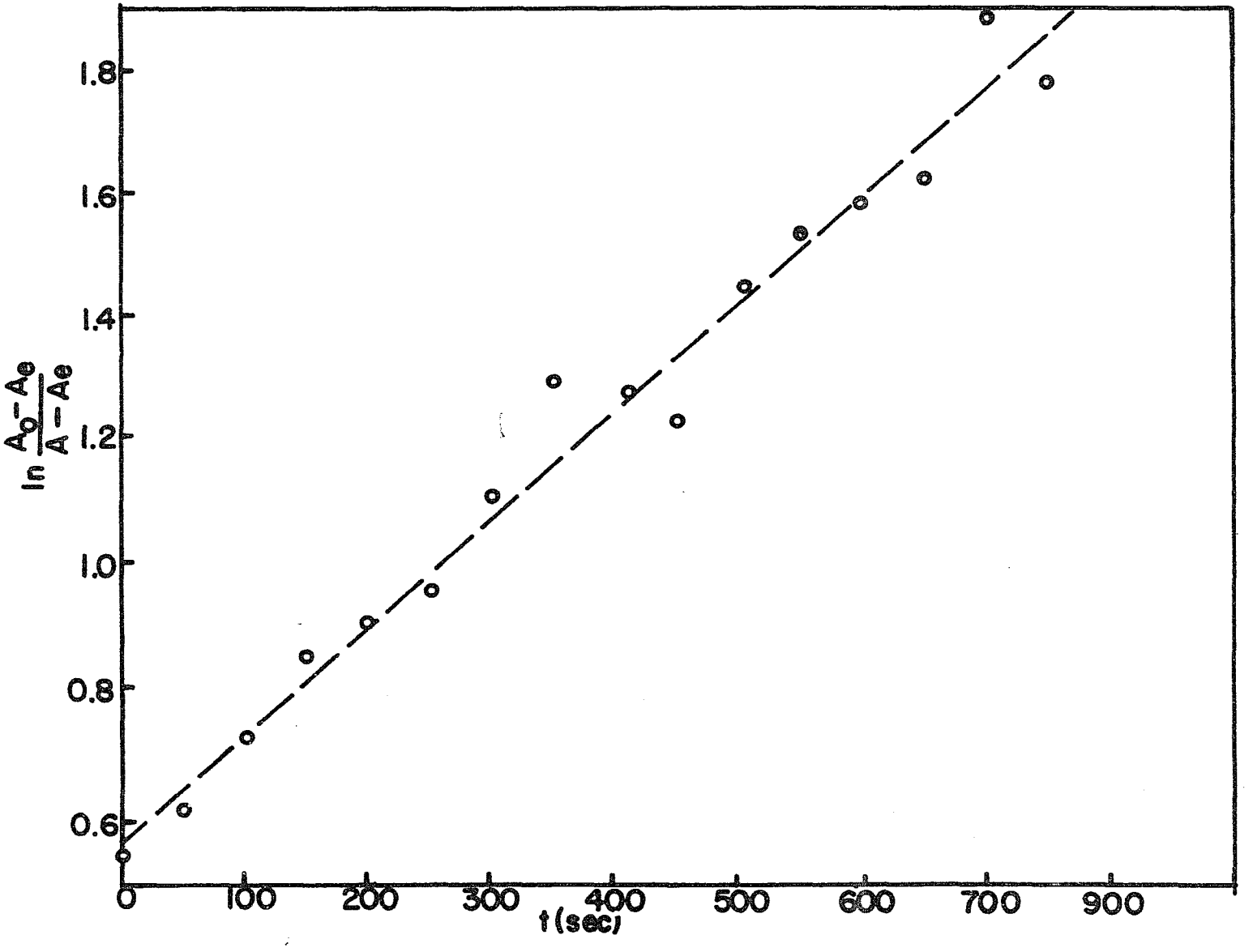


TABLE B-14

Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane[a] (7a) with 5.0×10^{-4} M HMPT in CCl_4 at 318°K.

Run 1			Run 2		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
0	126	35	0	123	33
50	120	36	50	116	36
100	116	40	100	116	40
150	109	46	150	112	41
200	109	46	200	111	45
250	110	51	250	105	45
350	103	49	300	110	46
400	101	56	350	108	47
455	106	56	400	105	55
500	101	59	450	107	53
550	100	63	500	100	54
612	94	63	550	101	55
673	98	65	600	100	55
700	94	64	650	94	56
750	93	65	700	93	58
800	89	67	750	91	62
850	91	71	800	92	66
			850	84	61

[a] 0.75 M in 7. [b] From NMR.

TABLE B-14a

Rate Constants Derived from Table B-14.

Run	$k' \times 10^3$, sec^{-1}	$k_1 \times 10^4$, sec^{-1}	r
1	1.44 ± 0.10	7.54 ± 0.52	0.990
2	1.25 ± 0.11	6.50 ± 0.57	0.982

FIGURE B-14. Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane with 5.0×10^{-4} M HMPT at 318°K. Data taken from Table B-14, run 1.

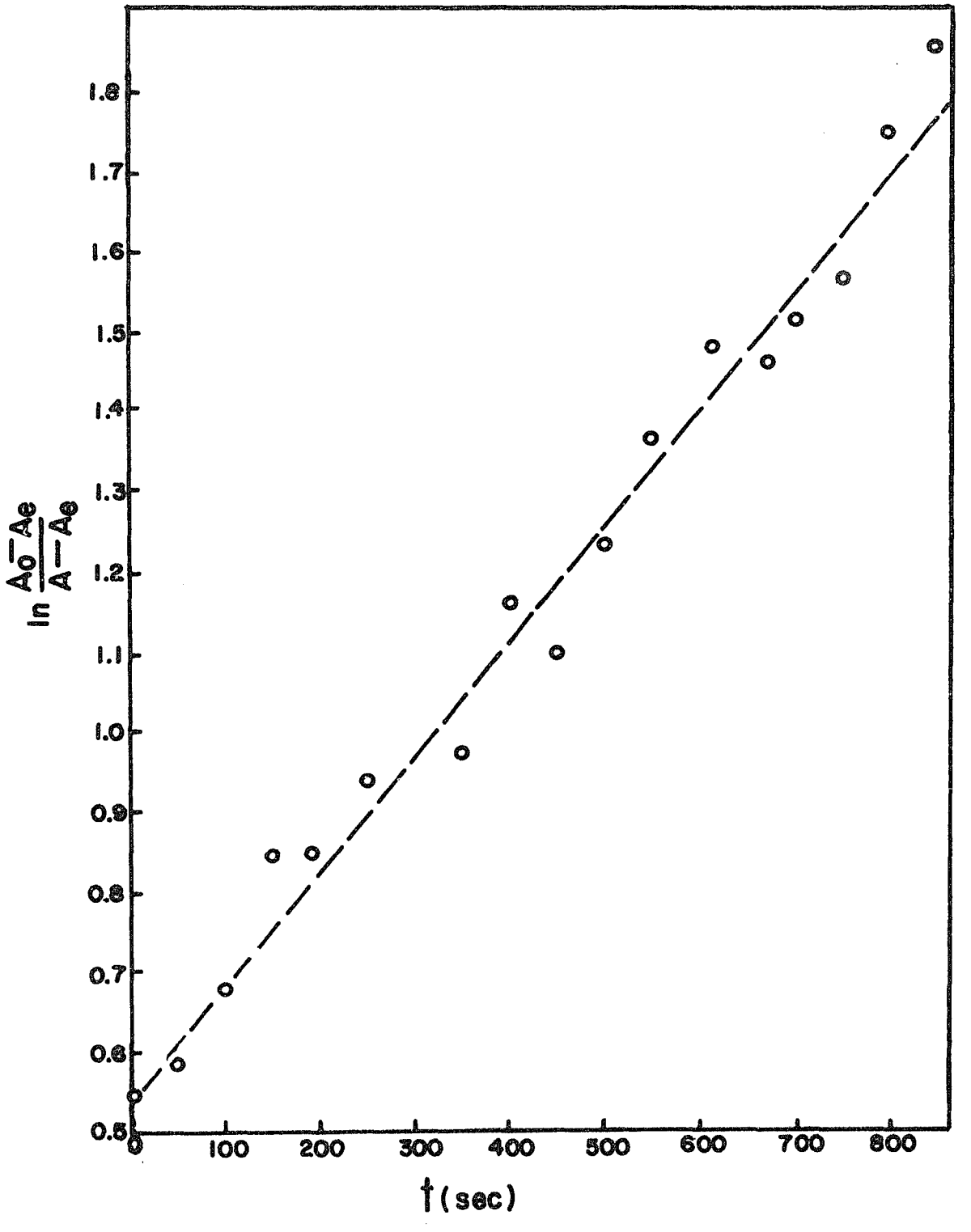


TABLE B-15

Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane[a] (7a) with 5.0×10^{-4} M HMPT in CCl_4 at 308°K.

Run 1			Run 1 (continued)		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
158	123	37	800	103	58
200	120	40	850	99	56
250	121	41	900	102	57
300	122	44	955	103	60
354	119	44	1015	100	57
400	116	45	1050	98	59
470	112	47	1100	97	60
550	110	51	1150	100	62
600	111	52	1250	96	61
650	109	54	1300	95	63
700	105	51	1350	93	61
750	100	51	1400	97	63

[a] 0.75 M in 7. [b] From NMR.

TABLE B-15a

Rate Constants Derived from Table B-15.

Run	$k' \times 10^4$, sec^{-1}	$k_1 \times 10^4$, sec^{-1}	r
1	7.10 ± 0.42	3.69 ± 0.22	0.989

FIGURE B-15. Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane with 5.0×10^{-4} M HMPT at 308^{o}K. Data taken from Table B-15, run 1.

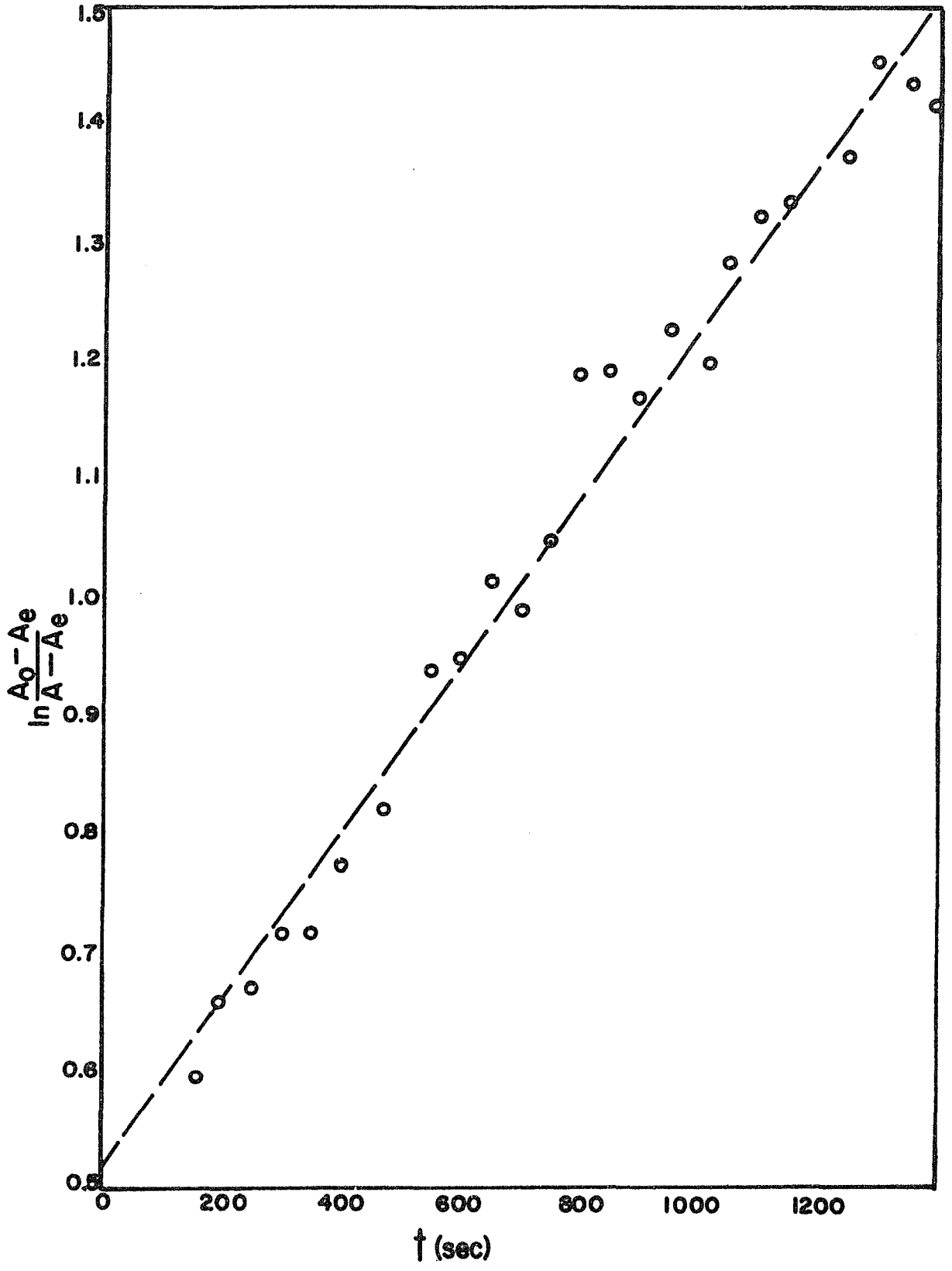


TABLE B-16

Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane[a] (7a) with 5.0×10^{-4} M HMPT in CCl_4 at 297°K.

Run 1			Run 1 (continued)		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
0	129	36	1300	117	57
50	129	37	1400	118	56
100	132	35	1500	116	56
150	130	38	1600	113	58
200	129	38	1700	107	61
300	129	41	1800	106	63
400	122	43	1900	112	63
500	121	45	2000	106	64
600	120	45	2100	106	63
700	115	48	2200	108	67
800	118	48	2300	101	67
900	114	50	2500	101	69
1000	113	50	2600	98	68
1100	115	55	2700	100	70
1200	111	55			

[a] 0.75 M in 7. [b] From NMR.

TABLE B-16a

Rate Constants Derived from Table B-16.

Run	$k' \times 10^4$, sec^{-1}	$k_1 \times 10^4$, sec^{-1}	r
1	3.82 ± 0.19	1.99 ± 0.10	0.991

FIGURE B-16. Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane with 5.0×10^{-4} M HMPT at 297°K. Data taken from Table B-16, run 1.

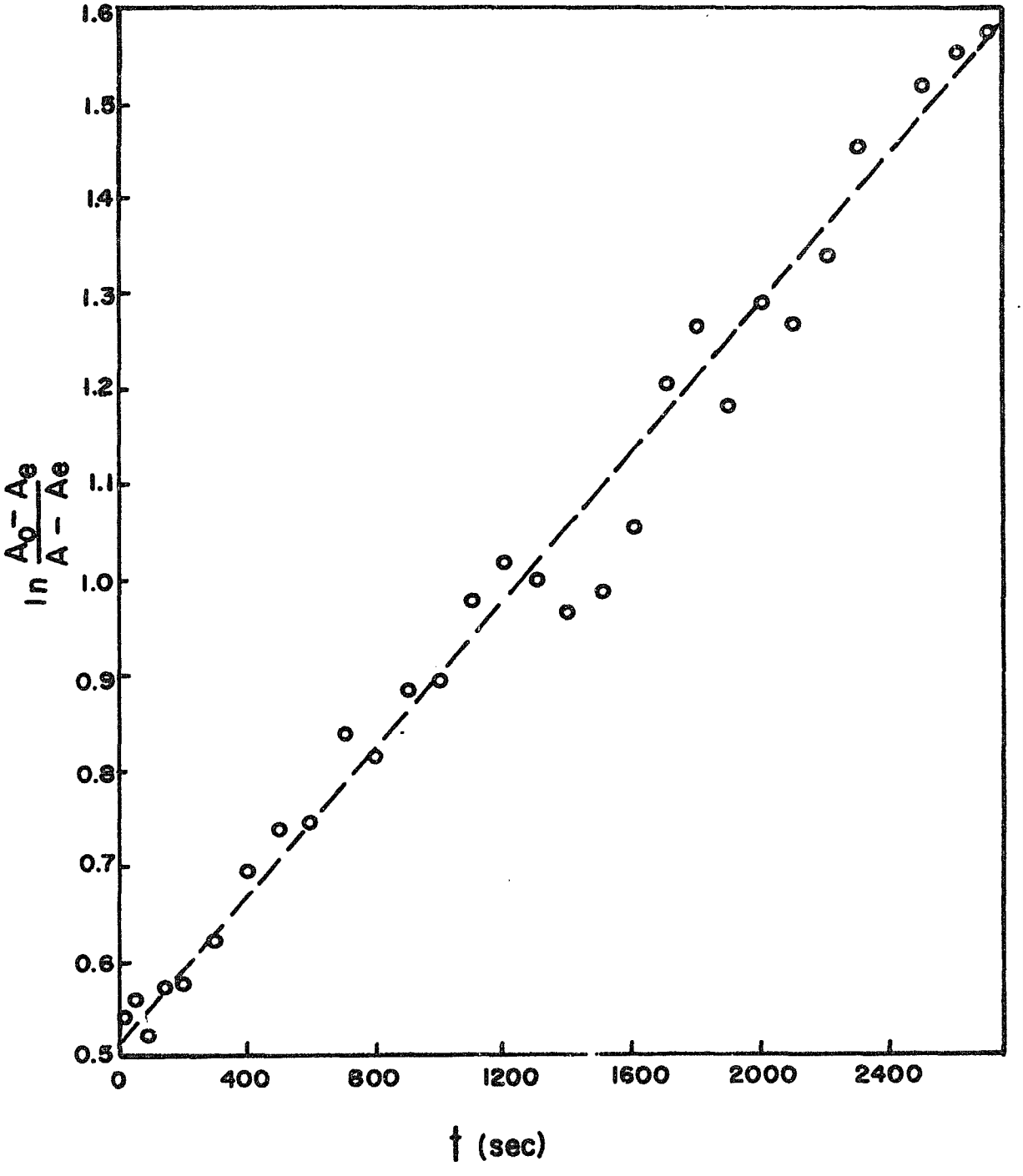


TABLE B-17

Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane[a] (7a) with 5.0×10^{-4} M HMPT in CCl_4 at 284°K.

Run 1			Run 1 (continued)		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
0	138	31	2600	128	48
50	141	31	2700	124	50
200	139	32	2800	121	49
400	137	35	3000	122	52
600	126	36	3200	116	55
700	128	40	3400	121	53
800	142	37	3600	116	53
900	130	40	3800	120	55
1000	129	39	4000	113	53
1200	131	40	4100	118	59
1400	128	42	4200	115	56
1600	135	42	4400	119	60
1800	125	46	4600	113	57
2000	129	45	4800	113	61
2200	120	50	5000	108	61
2400	122	48			

[a] 0.75 M in 7. [b] From NMR.

TABLE B-17a

Rate Constants Derived from Table B-17.

Run	$k' \times 10^4$, sec^{-1}	$k_1 \times 10^5$, sec^{-1}	r
1	1.36 ± 0.09	7.07 ± 0.45	0.984

FIGURE B-17. Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane with 5.0×10^{-4} M HMPT at 284°K. Data taken from Table B-17, run 1.

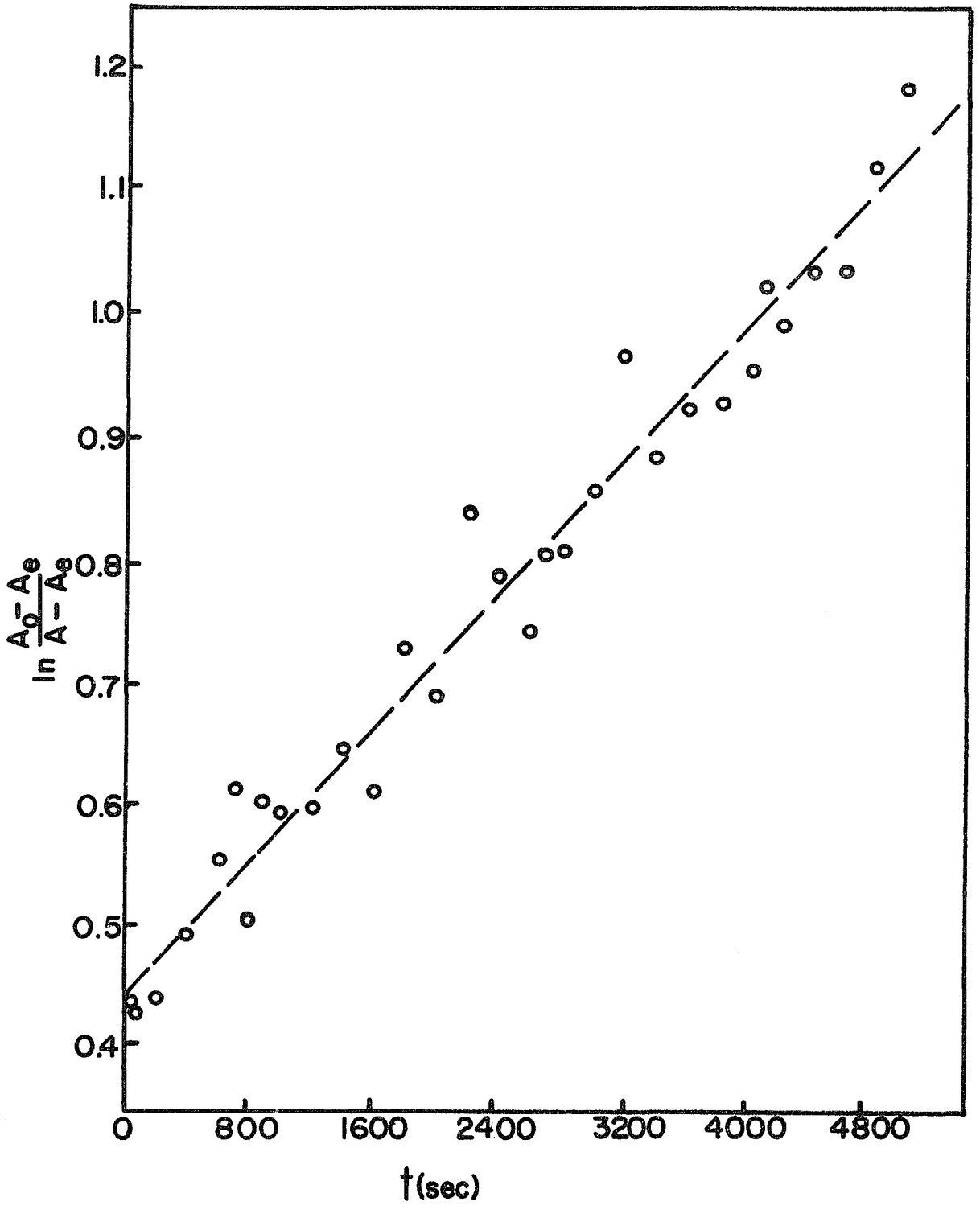


TABLE B-18

Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane[a] (7a) with 5.0×10^{-4} M HMPT in CCl_4 at 271°K.

Run 1			Run 1 (continued)		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
0	125	25	3000	117	35
25	123	26	3400	121	36
60	126	26	3600	118	36
100	124	27	3800	119	37
200	123	26	4000	120	37
300	123	27	4400	118	39
400	125	28	4600	116	37
600	123	28	4800	117	40
700	123	28	5200	115	40
800	124	29	5400	117	40
1000	119	30	5800	115	40
1130	122	30	6000	113	40
1200	126	29	6400	113	40
1400	123	30	6800	113	41
1800	126	32	7200	112	44
2000	121	33	7400	111	44
2200	119	34	7600	117	44
2400	125	35	7800	113	45
2750	116	35	8000	109	43
2800	119	36			

[a] 0.75 M in 7. [b] From NMR.

TABLE B-18a

Rate Constants Derived from Table B-18.

Run	$k' \times 10^5$, sec^{-1}	$k_1 \times 10^5$, sec^{-1}	r
1	4.81 ± 0.24	2.50 ± 0.12	0.988

FIGURE B-18. Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane with 5.0×10^{-4} M HMPT at $271^{\circ}K$. Data taken from Table B-18, run 1.

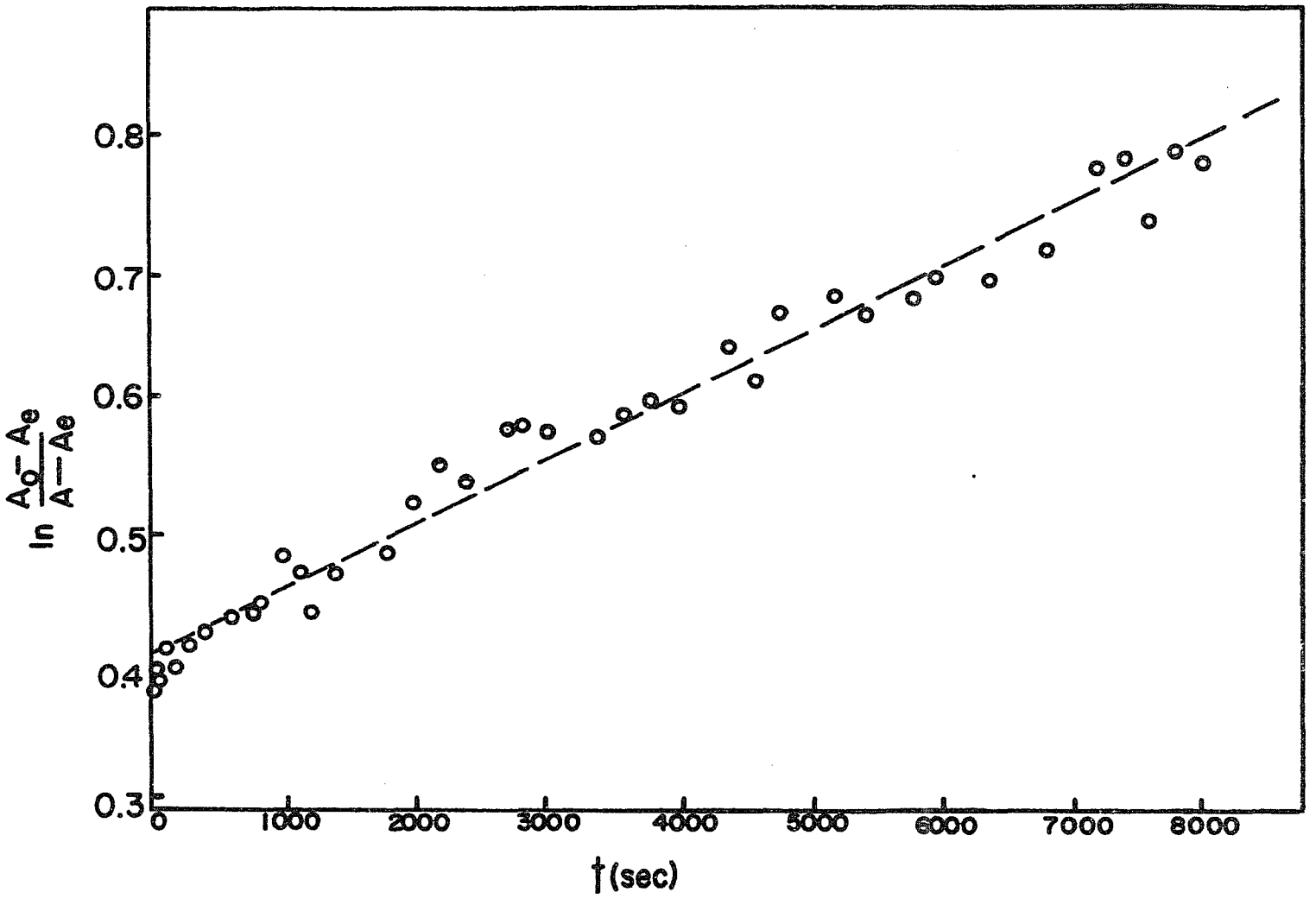


TABLE B-19

Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane[a] (7a) with 2.6×10^{-4} M Tetrabutylammonium Bromide in CCl_4 at 45°.

Run 1			Run 2		
Time, sec	Relative Area[b]		Time, sec	Relative Area[b]	
	7a	7b		7a	7b
335	114	43	0	119	37
400	111	43	50	117	36
500	111	48	100	120	40
600	109	51	160	114	41
700	106	51	200	120	43
800	100	53	250	120	45
900	103	56	300	117	45
1000	105	56	350	116	46
1100	103	60	400	115	47
1200	103	61	450	112	50
1300	97	61	500	116	50
1400	96	62	550	114	49
1500	96	66	600	112	50
1600	93	64	700	116	51
1700	94	64	825	105	53
1800	95	66	910	95	52
1900	93	64	1010	111	53
2000	89	67	1100	109	53
2100	88	71	1200	108	55
2200	89	69	1300	104	56
			1400	108	59
			1500	102	58
			1600	101	58
			1700	103	60
			1800	99	60
			1900	102	59
			2100	102	65

[a] 0.75 M in 7. [b] From NMR.

TABLE B-19a

Rate Constants Derived from Table B-19.

Run	$k' \times 10^4$, sec^{-1}	$k_1 \times 10^4$, sec^{-1}	r
1	5.82 ± 0.47	3.03 ± 0.24	0.984
2	3.42 ± 0.32	1.78 ± 0.17	0.972

FIGURE B-19. Isomerization of cis-1-Chloro-1,2-dimethyl-1-silacyclobutane with Tetrabutylammonium Bromide. Data taken from Table B-19, run 1.

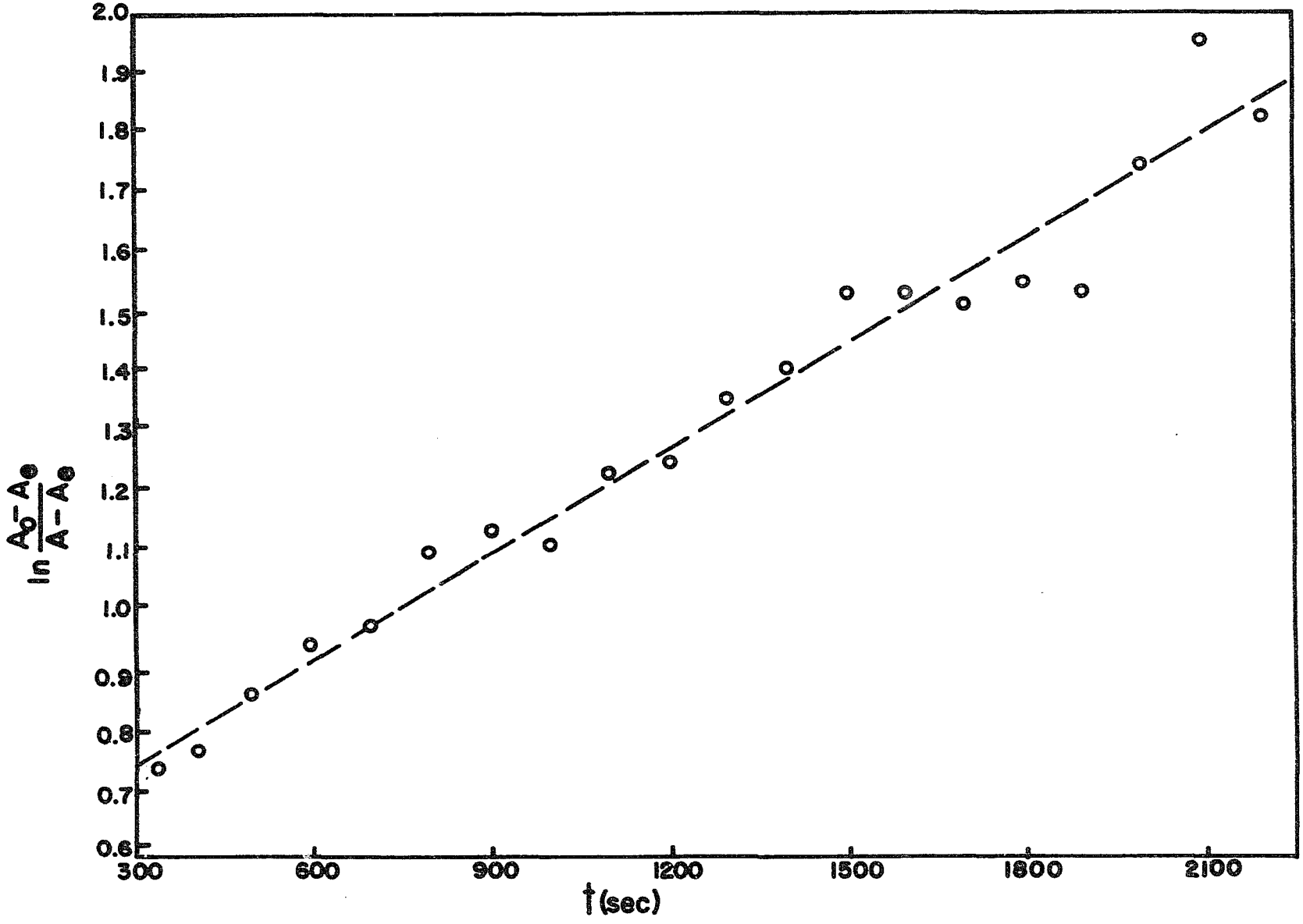
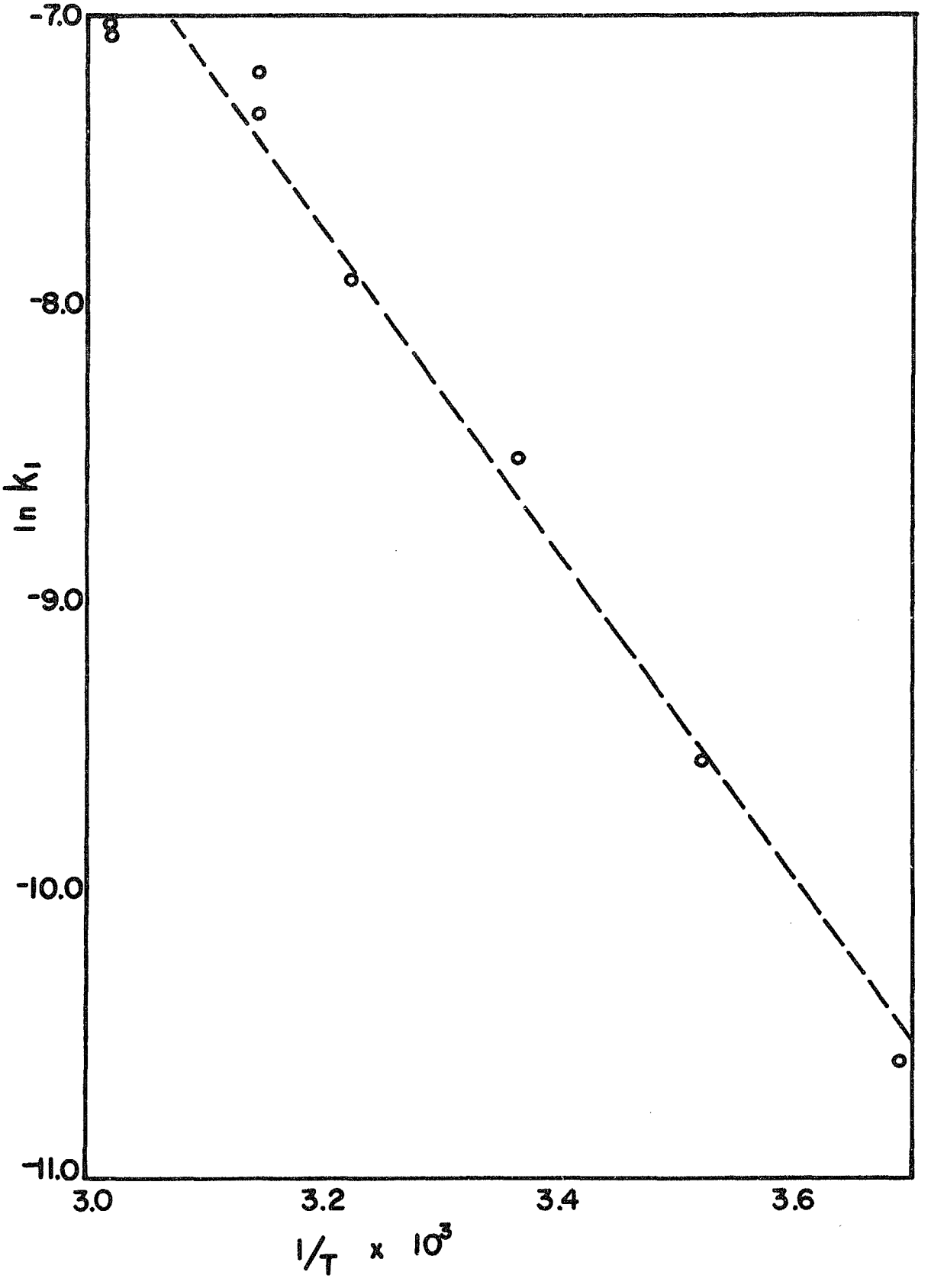


FIGURE B-20. Arrhenius Plot. Data taken from Tables A-13a through A-18a.



VITA

Bonnie Gary McKinnie was born on November 8, 1947, in Farmerville, Louisiana. He was educated at Linville High School in Linville, Louisiana, where he graduated in May, 1965.

He entered Louisiana Polytechnic Institute at Ruston, Louisiana, in the summer of 1965 and transferred to Northeast Louisiana State College in January, 1967, where he received the degree of Bachelor of Science in chemistry in May, 1969.

After serving two years in the U. S. Army he entered the Graduate School of Louisiana State University in Baton Rouge, where he is now a candidate for the degree of Doctor of Philosophy in chemistry.

On May 27, 1969, he married Faye Lois Criswell of Pollock, Louisiana. He is the father of one child, Amy Lynn.

EXAMINATION AND THESIS REPORT

Candidate: Bonnie Gary McKinnie

Major Field: Chemistry

Title of Thesis: Stereochemistry and Mechanisms of Reactions of Silacyclobutanes

Approved:

Frank K. Cartledge
Major Professor and Chairman

James D. Ingraham
Dean of the Graduate School

EXAMINING COMMITTEE:

Steven F. Watkins

William H. Daly

James Dale Macomber

K. N. Houk

Date of Examination:

July 17, 1975